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Attempts to Electrodeposit Magnesium at Ambient Temperature

B. Wines

January 1989

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ATTEMPTS TO ELECTRODEPOSIT MAGNESIUM AT AMBIENT TEMPERATURE:

An investigation of the usefulness of several non-aqueous solutions of magnesium salts as plating baths for magnesium electrodeposition

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Attempts to Electrodeposit Magnesium at Ambient Temperature:

An investigation of the usefulness of several non-aqueous solutions of magnesium salts as plating baths for magnesium electrodeposition.

by

Brian Wines

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ABSTRACT

Although magnesium possesses a standard potential which is less negative than those of the alkali metals, it has never been plated from non-aqueous electrolytes in a commercially useful manner. The present investigation was initiated in an attempt to find a suitable electrolyte for ambient temperature electrodeposition and dissolution of magnesium. The electrolytes studied include: propylene carbonate solutions of magnesium tetrafluoroborate and of aluminum chloride containing electrodissolved magnesium; magnesium tetrafluoroborate solutions in dimethyl sulfoxide and tetrahydrofuran; and a solution of magnesium bromide and aluminum bromide in toluene. Room temperature molten salts based on substituted imidazolium chlorides were also investigated. Several experiments were also performed at 100°C using dimethyl sulfone and sulfolane as solvents. Of these systems, only magnesium tetrafluoroborate in tetrahydrofuran gave a clean deposit of magnesium; however, this deposit was obtained at a much lower current density than can be obtained in the well-known deposition of magnesium from Grignard reagents. Magnesium anodes were roughened in all of the electrolytes studied, with the exception of magnesium tetrafluoroborate solutions in propylene carbonate, which yielded electropolished surfaces under the proper conditions. A review of previous attempts to electroplate magnesium from non-aqueous electrolytes is included.

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I. Introduction

Magnesium is a silvery white metal belonging to group IIA of the periodic table. Commercial applications of magnesium are based on the strong, light weight alloys it forms with other metals and on its high negative standard potential. Magnesium is also important in many organic chemical reactions as a component of Grignard reagents and is used to desulfurize iron and steel[1].

The metal was first isolated in 1808 by Sir Humphrey Davy, who produced an amalgam of the metal by electrolytic reduction of a mixture of mercuric oxide and magnesium oxide at a mercury cathode. A few years later, Bussey obtained free metallic magnesium by reacting magnesium chloride with metallic potassium. In 1833 Faraday produced the first magnesium obtained by electrolytic reduction of molten magnesium chloride. For many years after these initial experiments, magnesium was more of a laboratory curiosity than a commercially useful metal, but by the turn of the century a German magnesium industry had developed, based on the electrolytic reduction of the molten chloride. The magnesium industry in the U.S. was initiated by Dow Chemical in 1916 and by 1930 U.S. production had reached one million pounds per year. However, the U.S. magnesium industry did not develop in earnest until the early 1940's, when several plants were built in support of the war effort.

The electrolytic reduction of fused magnesium chloride remains the most common method of magnesium production; the major variations between the processes used by various manufacturers involve the methods of preparing the magnesium chloride feed stock for the electrolytic cell. Raw material for the refining process is obtained from dolomite, magnesite, and carnalite ores and from seawater, which contains large amounts of magnesium as the chloride salt. This last source makes magnesium the only structural metal with a virtually inexhaustible source in nature. The electrolytic cells must be run at temperatures well above 714°C to assure that the magnesium chloride feed stock remains molten. Magnesium is also produced by thermal reduction of the oxide. In the thermal reduction process, magnesium oxide, as a component of calcined dolomite, is reacted with a metal such as silicon to produce magnesium. These processes are run at about 1600°C and the refined magnesium is produced as a vapor[2].

With a specific gravity of 1.74, Magnesium is the lightest structural metal. The pure metal lacks sufficient strength for engineering applications, but alloys formed with aluminum, manganese, rare-earth metals, lithium, silver, thorium, zinc, and zirconium have very high strength-to-weight ratios. Magnesium alloys are widely used in the automotive and commercial aircraft industries[3].

Magnesium is high in the electromotive series, with a standard potential of -2.4 volts. Magnesium is often used as a sacrificial anode in the cathodic protection of steel structures. Despite the high value of magnesium's standard potential, it is resistant to atmospheric attack and certain chemical media because of its ability to acquire a protective film. This tendency to form surface films results in a working potential of 1.4 volts when magnesium is used as an anode in alkaline primary cells; the reduction of potential from 2.4 volts is due to IR losses across a protective magnesium hydroxide film. However, with an equivalent weight of 12.15, magnesium has one of the highest specific energies in the periodic table.

Since lithium, with a more cathodic standard potential of -3.04 volts, has been successfully used in non-aqueous rechargeable batteries, the barrier to using magnesium in a rechargeable cell cannot be a thermodynamic problem[4]. The present investigation was initiated as an attempt to electroplate magnesium at ambient temperature from a non-aqueous electrolyte. In addition to the use such a plating process would have in a magnesium secondary cell, ambient temperature electro-refining of magnesium might offer energy savings over the high temperature electro-refining currently used in the magnesium industry.

II. Review of Magnesium Electrodeposition Experiments

A. Early Experiments Using Grignard Reagents

Many attempts to electrodeposit magnesium have been reported in the literature since the first paper on the topic was published in 1912[5]. It is difficult to make meaningful comparisons between the work of various researchers active before the mid 1950's. Details of electrode size, cell potential, and current density are often given in a very sketchy manner. Solute and solvent purity are also difficult to compare, since these are rarely given much concern in the papers published before 1950. Also, it is only with the work of Brenner in 1956 that any serious attempt has been made to protect the electrodeposited magnesium from attack by water and air[6]. Finally, generally little attention was given to analyzing the quality of the cathodic deposits obtained in experiments.

The earliest case of magnesium deposition cited in the literature was the electrolysis of a Grignard reagent in ether by Jolibois in 1912[5]. He reported little more than the fact that the solution conducted and that magnesium formed at the cathode. The next reported electrodeposition of magnesium was published by Nelson and Evans in 1917[7]. This paper was the first of a series of papers on the electrolysis of Grignard reagents which Evans published with various coworkers over the following twenty-three years[8-14]. Magnesium electrodeposition was not the main purpose of this work; the study was undertaken as part of a growing interest in non-aqueous chemistry. The specific aim of the 1917 research was to determine if the etherates of magnesium alkyl halides (i.e. Grignard reagents) would increase the electrical conductivity of non-aqueous solvents like dry ether or benzene. The Grignard reagent was formed spontaneously in situ through the dissolution of the magnesium anode; platinum was used as the cathode. Depending on the size and spacing of the electrodes and the solution concentration (0.3 to 1.2 grams of magnesium as Grignard reagent per 100 ml of solution), a potential drop of 0.5 to 1.5 volts was obtained. The magnesium anode was believed to dissolve to form $(Et_2O)_xMgRX$. In the work that followed the first paper of the series, the cathodic deposition of magnesium continued to be of secondary importance to the study of the ether plating bath, with specific attention being payed to the nature of the electroactive magnesium species in the solution and the products of the anodic and cathodic reactions.

In 1934 a study was made by Evans which reproduced experiments conducted in the U.S.S.R. by Kondyrew[9]. Kondyrew used a mercury cathode in a Grignard solution to show that one Faraday of electricity reduced one equivalent of magnesium. Evans obtained the same result at a platinum cathode. Evans reported specific details of his experimental apparatus. 20 cm^2 platinum electrodes spaced 3 cm apart were used as cathodes and anodes. Applied voltage was varied between 80 and 110 volts to produce a current density of .02 amp/cm^2. The ether bath was refluxing during the experiment; this seems to have been the case for all the Grignard reagent electrolysis experiments conducted by Evans. While one mole of magnesium was being deposited at the cathode for each Faraday of charge, one mole of $MgBr_2$ was formed at the anode. Other than describing the deposit as spongy, no analysis of the deposit was reported. In some experiments aluminum anodes were used in place of the platinum anode. Unlike the chemically inert platinum anodes, the aluminum anodes dissolved to from $Al(C_2H_5)_3$.

By experimenting with various alkyl groups in the Grignard reagents, Evans found that larger alkyl groups lowered the applied potential at which magnesium would plate out[10]. Among isomeric radicals the relative magnitude of the deposition potential declined from 2.17 to 0.86 volt in the order primary> secondary> tertiary. In the next publication of the series[11], Evans concluded that there were no solvated Mg^+ ions present in the ether bath and suggested that the species reduced at the cathode was of the form RMg^+, where R is the alkyl group of the Grignard reagent. More attention was given to the nature of the cathodic deposit in a 1939 publication[13]. Working with 1.5 to 2.0 molar solutions of Grignard reagents in ether, Evans found that iso-propyl magnesium bromide gave different deposits than did n-propyl magnesium bromide. n-propyl magnesium bromide apparently yielded the spongy deposits described in earlier papers. The bath containing iso-propyl magnesium bromide yielded stringy deposits which adhered firmly enough to the cathode to resist being dislodged by the agitation of the refluxing solvent. Eventually the metallic strings would bridge the gap between the cathode and anode. The electrolysis lasted approximately 100 hours; apparently all of the preceding experiments conducted by Evans were of similar duration. The proposed cathodic reduction of a RMg^+ ion was again discussed, with the additional assumption that the oxygen atom of the ethyl ether solvent was coordinated with the magnesium atom of the unipositive ion. Evans further suggested that the cathodic reduction involved reduction of the coordinated solvent as well as the magnesium containing species.

In 1923 R. Muller et. al. published a paper on the electrolysis of magnesium bromide in pyridine[15]. Experiments were conducted with saturated solutions at 18°C and 60°C (0.5g/100g and 2.6 g $MgBr_2$/100g pyridine respectively). Both platinum and mercury cathodes were investigated. Magnesium deposited on the platinum cathode in the form of a grey coating which reacted to form H_2 when dipped in hydrochloric acid. If the electrolysis was interrupted, a coherent film formed rapidly over the cathodic deposit; this film hindered further electrodeposition when the electrolysis was resumed. The film appears to have been produced by the reaction of the deposited metal with pyridine. At 18°C the current density and applied voltage were 3×10^{-4} amp/cm^2 and 3 volts. The magnesium deposit was analyzed by comparing its potential versus a silver-pyridine reference electrode with the potential of a pure magnesium sample versus the reference electrode. In both cases the potential was 1.35 volts. Curiously, deposition on a mercury cathode was found to be more difficult than on a platinum cathode. The current density was 4×10^{-4} amp/cm^2 and the potential relative to the silver-pyridine reference electrode was 1.65 volt, or 0.3 volt greater than the potential required to deposit magnesium on the platinum cathode. This potential was reported to correspond well with that measured on a dropping mercury electrode (DME) using a magnesium amalgam in place of mercury. The applied voltages for the above experiments were approximately 10.5 volts.

Further work with the electrolysis of Grignard reagents was reported by Kondyrew in 1925[16]. Dry ether was used as the bath solvent, platinum as the cathode, and aluminum, zinc, copper, magnesium, or iron as the anode. Deposition experiments were performed at ambient temperature. Kondyrew did not report the applied voltage used in the experiments. When a magnesium anode was used, a deposit of metallic magnesium appeared on the cathode. During some of the experiments dendritic deposits grew large enough to bridge the cathode-anode gap. Of the metals used as anodes, only zinc, aluminum, and magnesium would go into solution. With a zinc anode, the cathodic deposit initially consisted of magnesium from the Grignard reagent and eventually became covered with a zinc deposit. When aluminum was used as the anode, only the magnesium from the Grignard reagent was observed at the cathode, although the bath conductivity did increase as the aluminum went into solution.

The cathodic electrodeposits obtained by Kondyrew were described as spongy layers composed of shiny platelets. Several chemical tests were performed on the deposits to determine their nature: flakes from the deposit were found to have a density of less than 2.19; when the deposit was burned a voluminous oxide was formed which was found by chemical analysis to be MgO; and when the deposit was dissolved in a solution of ethyl bromide in ether, a violent reaction occurred in which the deposit was completely consumed. Based on these results Kondyrew concluded that the deposit was composed solely of magnesium.

Further studies using Grignard reagents were published by French in 1927 and 1930[17,18]. In the earlier study two platinum electrodes (5 cm^2, 2 cm separation) were used in ether baths of phenyl magnesium chloride or benzyl magnesium bromide. 110 volts DC was applied and the current density was 4×10^{-4} amp/cm^2. The energy dissipated in the baths caused them to boil vigorously. A deposit began to form within a few minutes of the start of electrolysis. After completion of the experiment, the deposit was rinsed with ether and analyzed. In cold water the deposit reacted exothermally to form magnesium hydroxide. In ether solution the deposit could be reacted with alkyl halides to form Grignard reagents. The amount of magnesium recovered was determined by dissolving the deposit in excess sulfuric acid and back titrating with alkali. In benzyl magnesium chloride based baths magnesium was found to plate with almost 100 percent current efficiency, while in phenyl magnesium chloride based baths the current efficiency was less than 10 percent. Like Evans, French concluded that magnesium bromide was formed at the anode.

In the second set of experiments, 10 cm^2 platinum cathodes were paired with 20 cm^2 anodes of aluminum, tin, cadmium, zinc, bismuth, gold, silver, and nickel. Experiments were run at 110 volts applied potential with currents between 10 and 20 milliamperes for about 200 hours. In all cases a light, bushy deposit of magnesium began to form at the cathode within a few minutes of starting the electrolysis. In some cases the deposit bridged the cathode-anode gap. Of the anodes used, only aluminum, zinc, and cadmium were attacked during electrolysis and of these three only aluminum was found to go into solution, although aluminum was not detected in the cathodic deposit.

Rodebush and Peterson conducted experiments similar to those of French[19]. Baths composed of Grignard reagents in ethyl ether were subjected to 110 volt applied potentials between platinum electrodes. Beautiful, crystalline, adherent deposits were reported, but no chemical analysis of the deposits was given.

In 1931 Audrieth and Nelson published a review of the efforts to electrodeposit metals from non-aqueous solvents[20]. In addition to referencing the work by Muller and Evans, they discussed some general problems of metal deposition in non-aqueous solvents. One of these is the role of trace water in the electrolyte. Audrieth and Nelson reported that the effect of water depends greatly on the solvents and salts used: in some cases no effect is observed; in others the deposition of the metal is hindered, but the character of the deposit obtained is improved. Reference is also made to the difficulty of predicting the usefulness of a particular solvent for electrodeposition; at one time it had been thought that the dielectric constant was the most important parameter, but it was found that, given the proper solute, practically any solvent may act as an ionizing medium.

Overcash and Mathers experimented with both simple salts of magnesium and Grignard reagents[21]. The cells they used contained platinum cathodes (8.5 cm^2) and magnesium anodes (6.46 cm^2) and were sealed with cork stoppers to prevent free access of air to the bath. Attempts at plating were made with magnesium bromide, magnesium thiocyanate, magnesium perchlorate, magnesium ethylate, and magnesium methylate in pyridine, formamide, benzonitrile, acetonitrile, o-toluidine, aniline, ethyl bromide, dimethylaniline, and ether. None of these baths yielded a cathodic deposit.

As a departure form earlier research with Grignard reagents, Overcash and Mathers attempted to find additives which would stabilize the baths and improve deposit character. Electrolysis with various additives was performed using a 110 volt source of applied potential and a current density of 2 x 10^{-4} amps/cm^2. Benzene, toluene, xylene, quinoline, pyridine, ethylene bromide, ethylene dichloride, ethyl acetate, dimethyl sulfate, amyl alcohol, monochlorobenzene, and tetrachlorobenzene were all tried as additives, at concentrations amounting to about 20 percent of the bath volume, without giving any improvement in the magnesium deposits obtained. Primary amines were also tried because they were known to combine with Grignard reagents:

$$RMgX + RNH_2 = RH + RNHMgX$$

Aniline, o-toluidine, beta-naphthylene, and dimethylaniline were all tried: dimethylaniline was found to give the best results. Using dimethylaniline in the bath, it was possible to run the electrodeposition at 20 volts and a current density of 6 x 10^{-3} amp/cm^2. In the course of time the voltage required to maintain the current density increased and the bath was of no use after a total of 30 hours of electrolysis. The deposits were described as light grey, crystalline, and adherent, but became treed if the deposition was carried on for any length of time. If the current density was increased the deposits became darker and less adherent. The presence of dimethylaniline in the bath helped to suppress treeing. Overcash and Mathers also found that Grignard reagents containing iodine gave whiter, more finely crystalline, more adherent deposits than Grignard reagents containing bromine. Grignard reagents made with larger alkyl groups produced less satisfactory plating baths. In contrast to the findings of Kondyrew[16], no dissolution of the magnesium anode was observed. When the cathodic deposits were exposed to air a white film formed on their surface, which could not be removed by dry ether, alcohol, ethyl bromide, or dimethylaniline, but was removed by washing with water. During the water washing of the film, hydrogen was generated. The amount of magnesium deposited was determined by dissolving the deposit in nitric acid, evaporating the solution to dryness, and igniting the sample to MgO, which was then weighed. It is therefore impossible to say what percentage of the deposit was actually composed of magnesium, since any organic material included in the deposit would have been destroyed in the analysis procedure. A cathodic current efficiency of 55% was reported.

B. Experiments Using Magnesium Salts in Non-Aqueous Solvents

Dirkse and Briscoe attempted to plate several metals from non-aqueous solvents[22]. 1 cm^2 platinum anodes and a 110 volt applied potential source were used. Magnesium electrodeposits could not be obtained from magnesium salts in acetamide, nitrobenzene, aniline, acetone, benzoyl chloride, or glacial acetic acid. A smooth cathodic deposit was obtained on a copper cathode in a bath of magnesium nitrate in mono-ethanolamine, which had been electrolyzed at 0.3 amps for 15 minutes. No chemical analysis of the deposit appears to have been performed.

In the 1950's Brenner, at the National Bureau of Standards, performed many experiments on the electrodeposition of metals from organic solutions. In the first paper published on this research program, considerable attention was given to establishing the necessary features of a good plating bath[6]. Only certain classes of solutes and solvents were found to form plating baths, and Brenner concluded that a successful plating bath required the formation of a loose ionic complex between the solute and the solvent. In the absence of the complex no conductivity occurs. If the complex between solute and solvent is too stable, conductivity may occur, but not metal deposition. The complexes that ionize to give a conducting solution often exist only in solution. Brenner found that only four classes of solutes gave any promise of successful depositions: halides, hydrides, borohydrides, and organometallic compounds (Grignard reagents). Of these compounds the halides and organometallic compounds had been used in the work of earlier researchers, while the hydrides and borohydrides represented a new contribution to the field by Brenner's research team. It was also found that combinations of solutes gave better plating baths. For example, the hydride aluminum plating bath required both $AlCl_3$ and aluminum hydride. These solutes contain no oxygen or nitrogen. Brenner found that solutes in which the metal atom is bonded to oxygen or nitrogen did not yield deposits of aluminum, beryllium, magnesium, titanium, or zirconium; apparently the bond between the metal and oxygen or nitrogen is too strong. The failure to obtain deposits from perchlorates was attributed to this effect. It was also found that solutes which worked well for one metal did not necessarily give good results for others; chloride-hydride plating baths yielded good electrodeposits of aluminum, but very poor electrodeposits of beryllium or magnesium. The only solvents which yielded electrodeposits were ethers and aromatic hydrocarbons. The failure of such solvents as alcohols, ketones, acids, acid hydrides, amides, amines, and nitriles was attributed to the formation of too stable complexes with the solute. Ether based baths were thought to give the best results because the oxygen atom coordinated sufficiently, but not too strongly, with members of the four solute types mentioned above. Brenner's attempts to electrodeposit pure magnesium were not successful[23]. Using a plating bath of magnesium borohydride in ether, he obtained deposits which were an alloy of magnesium and boron. A feature unique to Brenner's work was the first reported use of an inert atmosphere to protect the plating bath from moisture or air.

At about the same time that the Brenner papers were published, Connor, Reid, and Wood published the results of their attempts to electrodeposit magnesium and magnesium alloys[24]. Like those of Brenner, these experiments were conducted in an inert atmosphere. All deposits were made on copper cathodes. Aluminum anodes were used because they were easier to dissolve than magnesium and because magnesium anodes decomposed the baths more rapidly than aluminum anodes. It was assumed that none of the aluminum was codeposited with magnesium at the cathode since all of the aluminum from the anode could be accounted for in the plating bath. Connor et. al. worked with baths based on magnesium bromide. Magnesium chloride was considered, but discarded when it was found to be virtually insoluble in ethyl ether. Benzene, phenyl ether, dioxane, phenetol, anisole, triethylamine, xylene, and cyclohexylamine were tested and found to be poor solvents for magnesium bromide. Tetrahydrofuran, pyridine, and N,N-diethylacetamide formed precipitates with magnesium bromide at room temperature. When tetrahydrofuran was used in a plating bath at its boiling point, a black, powdery deposit was formed at a current density of 0.012 amp/cm^2; at lower current densities no deposits were formed. For the bulk of the work, ethyl ether was the only solvent used.

When magnesium bromide is added to ethyl ether in concentrations exceeding three percent by weight, two liquid layers form. The lower layer is about thirty nine percent by weight magnesium bromide (about 2.5 molar). If the bath temperature goes below 21°C, $MgBr_22Et_20$ crystallizes out from this layer. When the lower layer was electrolyzed dark, brittle deposits were obtained which contained between sixty and seventy percent magnesium. The remainder of the deposit was thought to include oxide and organic matter occluded from the bath. Good deposits were hard to build up because of excessive treeing. Adding $LiBH_4$ to the bath in a 1:4 molar ratio to the $MgBr_2$ improved solution conductivity and gave a smooth dense deposit. With equimolar amounts of $LiBH_4$ and $MgBr_2$ a sound metallic deposit was obtained, but treeing occurred and it was difficult to obtain a thick deposit. When the ratio of $LiBH_4$ to $MgBr_2$ was increased to 2:1 a smooth bright deposit was formed, but treeing was still a problem. All of the experiments with $LiBH_4$ were conducted at a current density of 0.01 amp/cm^2. In all three cases the deposits were ninety percent magnesium and ten percent boron. Adding thiophene to the baths reduced treeing, but also lowered conductivity and hurt the stability of the bath.

Magnesium deposits were also obtained from Grignard reagents. 2.5 molar ethyl magnesium bromide in ethyl ether was electrolyzed at a current density of 3×10^{-3} amp/cm^2 and an applied voltage of 50 volts. The resulting deposits appeared white and metallic, but were actually only seventy percent magnesium. An attempt to suppress treeing by rotating the cathode was unsuccessful. Adding $LiBH_4$ to the Grignard reagent bath also failed to improve the deposit.

Of the various attempts to plate magnesium alloys, the most interesting cases involved baths of $MgBr_2$ in ethyl ether with $LiAlH_4$ added in a 0.2:1 or 0.08:1 molar ratio of $LiAlH_4$ to $MgBr_2$. Both of these baths gave white coherent deposits which were ninety percent magnesium and ten percent aluminum.

Brenner's most recent paper on magnesium electrodeposition was published in 1971[25]. At that time it was claimed that a plating bath had been developed which deposited smooth, white, somewhat ductile coatings of magnesium. The bath was prepared by slowly adding a saturated solution of 1 gram of decaborane dissolved in anhydrous tetrahydrofuran to 25 ml of a commercially obtained 1.7

molar solution of lithium methyl in diethyl ether. After combination of the two solutions a heavy, yellow layer containing most of the lithium separated out of the bath. The lower layer had a much higher conductivity than the upper layer. The bath was completed by adding 25 ml of a saturated solution of magnesium chloride in anhydrous tetrahydrofuran. With the addition of the magnesium chloride solution the bath became homogeneous and possessed a greater conductivity than the two phase bath. Brenner believed that the unidentified magnesium complex formed in the bath was approximately one molar. The preparation and operation of the bath were performed in an argon atmosphere.

When the completed bath was electrolyzed at 1×10^{-3} to 1×10^{-2} amp/cm^2 a smooth, white, sound deposit of magnesium was formed on the cathode. Tubes of this deposit were electroformed by deposition on thin-walled aluminum tubing, followed by dissolving out the aluminum with caustic soda. The deposit was not analyzed, although Brenner believed that it contained no more than one percent Boron. Unfortunately, an analysis of the deposit was not subsequently published.

An alternative method of bath formation using Grignard reagents was also described. One gram of decaborane was added to 60 ml of a tetrahydrofuran solution of magnesium ethyl chloride. 25 ml of magnesium chloride in tetrahydrofuran was added to this solution to complete the bath. This second bath yielded electrodeposits, but was not as effective as the bath formed with lithium methyl.

Several attempts at magnesium electrodeposition in this laboratory were reported by Jorné in his dissertation[4]. His experiments were performed using

100 ml baths of magnesium salts in propylene carbonate (water content in the PC reported as less than 40 ppm) and were conducted in an argon atmosphere. The various salts used by Jorné were dried at pressures of less than 50 microns and temperatures greater than 200°C. Electrodeposition experiments were performed in an H cell with a glass frit between the chambers. Magnesium rods or platinum foils were used as anodes and platinum foils were used as cathodes. Typical deposition experiments lasted a few hours and were performed galvanostatically at current densities of 1×10^{-3} to 1×10^{-2} amp/cm^2. The most promising deposits were washed with propylene carbonate and then dissolved in dilute nitric acid for spectral analysis of magnesium, lithium, potassium, and boron content. A few deposits were also analyzed by X-ray diffraction. In most cases the deposits were thin enough that peaks corresponding to the platinum substrate had to be subtracted from the X-ray diffraction data.

$MgCl_2$, $MgBr_2$, and MgI_2 gave no deposits. Attempts to complex these halide salts with $AlCl_3$ resulted in yellow deposits on the cathode. Similarly, attempts to complex MgF_2 with $AlCl_3$ or BF_3 failed to produce metallic deposits. $Mg(ClO_4)_2$ gave unstable black deposits when dissolved by itself or in the presence of $AlCl_3$. $NaBH_4$ was also used as a co-salt for magnesium salts: with MgI_2, $MgCl_2$, and MgF_2 metallic deposits were not obtained; with $Mg(ClO_4)_2$ the resulting deposit contained equal amounts of magnesium and sodium. Solutions of $NaBF_4$ and $Mg(ClO_4)_2$ also produced deposits with equal amounts of magnesium and sodium; substituting KBF_4 or KPF_6 for $NaBF_4$ resulted in deposits of potassium. $LiBH_4$ in combination with $MgCl_2$ or $MgBr_2$ produced cathodic deposits with three times more lithium than magnesium; in combination with $Mg(ClO_4)_2$ deposits with four times more magnesium than lithium were formed. The most likely deposit of magnesium was obtained from a solution of $Mg(BF_4)_2$; this grey deposit was analyzed by X-ray diffraction, after exposure to air, and found to contain MgO. Jorné was not sure if the MgO had been produced in the plating bath or only after exposure to air. $Mg(NH_4)Cl_3$, $MgMoO_4$, $MgWO_4$, and $MgTiO_4$ were all found to be insoluble in propylene carbonate.

Although none of the deposits were found to be 100 percent magnesium, the best results were obtained from baths in which the anion included boron. This agrees with Brenner's observation[6] that the borohydrides gave the best magnesium electrodeposits in ether plating baths. Jorné also attempted to plate using magnesium borohydride, but the synthesis procedure he used resulted in small amounts of lithium remaining in the salt. When this sample of magnesium borohydride was electrolyzed, the deposit was eighty percent lithium.

Attempts to plate magnesium out of dimethyl sulfoxide, pyridine, di-ethyl ether, and tri-ethylene-glycol-dimethyl ether using magnesium halides, $Mg(ClO_4)_2$, and $Mg(NO_3)_2$ were unsuccessful.

In 1988 Gregory et. al. [26] reported the development of an ambient temperature secondary magnesium battery. The cell consists of a solid magnesium anode and a cathode made of a transition metal oxide, sulfide, or boride. Magnesium was found to reversibly intercalate in transition metal compounds; ZrS_2, RuO_2, Co_3O_4,

Mn_2O_3, and V_2O_5 are reported to have capacities of at least 0.2 Ah/g and potentials of at least 2.2 volts versus magnesium. Grignard reagent based electrolytes are reported to be capable of both electrode reactions with 100 percent current efficiency and the magnesium plated on the anode during charging is described as a bright, compact, crystalline metal of greater than 99.95% purity. Operation of a cell with a Grignard reagent based electrolyte failed as a result of reactivity between the electrolyte and the cathode. Successful cells were operated using electrolytes of magnesium bis-organoborates ($Mg(BR_4)_2$) in ethers. This electrolyte is similar to the electrolyte used in some rechargeable Li/TiS_2 cells[27]. A charge-discharge cycle of the system:

$$\mathrm{Mg}|0.25\ \mathrm{M\ magnesium\ dibutyl\ diphenyl\ borate\ in\ THF}|\mathrm{Co_3O_4}$$

is reported, for which the operating voltage is only 0.35 volt. The authors speculate that the functioning of this cell is a consequence of the Mg-B bond in $Mg(BR_4)_2$ compounds possessing both covalent and ionic characters; covalency being necessary for magnesium plating and ionizable compounds being required for the cathodic intercalation reaction.

III. Electroreduction of Alkali and Alkaline Earth Metals in Non-Aqueous Media

A. General Background

In non-aqueous electrochemistry it is often difficult to compare the work of different authors. Experiments usually differ in the choice of solvents, supporting electrolytes, working electrodes, and reference electrodes used. A uniform reference potential would be especially helpful since the reduction potential of a cation reflects the degree of difficulty involved in removing the cation from a given electrolyte. Two of the more common reference electrodes used in the study of alkali metal and alkaline earth cations are the Ag|Ag$^+$ electrode and the saturated calomel electrode (SCE). The Ag|Ag$^+$ electrode is most commonly of the form Ag|AgCl, but this form is incompatible with some non-aqueous systems; in propylene carbonate (PC) there is a strong solvent interaction with AgCl, resulting in increased AgCl solubility and an unstable reference potential[28]. To avoid the AgCl solubilization, $AgNO_3$ is sometimes used in place of AgCl. It has also been reported that there is a photo-induced reaction between PC and silver ion[29].

A significant drawback to the use of the calomel electrode in non-aqueous studies is the unavoidable introduction of water from the reference electrode into the non-aqueous solvent. In experiments using dropping mercury electrodes (DME) this does not seem to be a serious drawback, as concentrations of water of up to 0.1% are reported to have no detectable effect on the reduction. This is probably a result of two effects: the nature of the DME, with its constantly renewed surface, prevents any significant reaction between water in the solution and the reduced metal in the mercury and, as long as the water concentration is sufficiently low, the majority of the cations should have primary solvation shells composed almost entirely of non-aqueous solvent molecules. Brown and McIntyre report that in DMF with less than 200 ppm water there is essentially no water in the primary solvation shell of Mg^{2+}[29]. At water concentrations of 1% in N,N-dimethylacetamide(DMA) this second condition is clearly not met since Gutman reports that 1% water in DMA is necessary to produce polarographic reduction waves for Mg, Ca, Sr, and Ba[30]. This behavior is attributed to the presence of water in the primary solvation shell of the cations; the authors suggest that the unsymmetrical solvation shells containing both non-aqueous solvent and water molecules are easier to desolvate at the cathode. At water concentrations in excess of 3% the cation reduction is hindered.

Matsuura et. al. have used the SCE as a reference in measuring the polarographic half wave potentials of alkali metals in several non-aqueous solvents. The potentials measured in the solvents were normalized to the potential of SCE in aqueous solution by making corrections of potential required for transfer of rubidium ion from water to the solvents. The corrected potentials at a dropping mercury electrode and the solid metal are given in Table 1. A general trend of increasingly cathodic potentials with higher solvent donor number can be observed from this data[31,32]. Table 2 is reproduced from Gutman et. al., who measured the half wave potentials of alkali and alkaline earth cations at a DME in PC

Table 1. Standard Potentials of the Alkali Metals at Alkali
Metal and Dropping Mercury Electrodes
0.1 M TEAP or TBAP as supporting electrolyte
(Volts cathodic of SCE)

	Water	PC		EC	DMF		DMSO	
Solvent Donor Number	33	15.1		16.4	26.6		29.8	
	DME	metal	DME	DME	metal	DME	metal	DME
Li	2.339	2.906	2.039	2.046	3.163	2.425	3.327	2.688
Na	2.114	2.691	1.854	1.862	2.830	2.035	2.898	2.075
K	2.140	3.002	1.970	1.986	3.067	2.060	3.116	2.095
Rb	2.140	2.980	1.991	2.009	3.040	2.050	3.079	2.075
Cs	2.128	2.986	1.982	2.046	3.048	2.013	3.079	2.050

Matsura,Umemoto,Waki,Takeuchi,Omoto,Bull.Chem.Soc.Japan,47(4),806(1974)
Matsura,Umemoto,Takeuchi,Bull.Chem.Soc.Japan, 47(4), 813 (1974)

Table 2. Half Wave Potentials for Alkali and Alkaline Earth Cation
Reduction at a Dropping Mercury Electrode in Propylene Carbonate
(0.1 M TEAP supporting electrolyte SCE reference)

Alkali Metal	E½	Alkaline Earth Metal	E½
Li*	-1.99	Be*	-1.60
Na	-1.96	Mg*	-1.72
K	-1.84	Ca*	-1.92
Rb	-1.97	Sr	-1.83
CS	-1.97	Ba	-1.67

* irreversible
Gutman,Kogelnig,Michlmayr,Monatscheft fur Chemie,99,643(1968)

Table 3. Standard Potentials of the Alkali Metals in
1.0 m $AlCl_3$ in Propylene Carbonate and Pure Propylene Carbonate
(Volts cathodic of TlCl/Tl reference)

	1m $AlCl_3$	Pure PC
Li	2.045	1.850
Na	1.885	1.691
K	2.116	1.922
Rb	2.116	1.992
Cs	2.122	1.928

J. Jorné, Electrochemical Behavior of the Alkali Metals in Propylene
Carbonate, Ph.D. Thesis, Dept. of Chem. Engr., U.C. Berkeley (LBL-1111)(1972)

solution[33]. No correction for liquid junction potential between water and PC was made for this data. The magnesium half wave potential is 0.27 volts anodic of the lithium half wave potential; this indicates that the barrier to successful magnesium plating is not thermodynamic.

Another reference electrode which has been used with success in non-aqueous electrochemistry is based on thallium halide salts in contact with thallium amalgams. These electrodes give very reproducible potentials and are stable over long periods of time[4,28,34,35]. Since the electrode potential is sensitive to the thallium concentration in the amalgam, the experimentally measured potentials are often reported with respect to solid thallium in contact with the thallium salt by adding the potential difference between the solid and the amalgam to the calculated standard potential of the experimental cell. The use of actual Tl|TlX electrodes has been reported[28], but they are not as durable as the amalgam electrodes. Table 3 contains the standard potentials of the alkali metals in PC with respect to a TlCl|Tl reference electrode as determined by Jorné[4]. Jorné measured the potentials of the alkali metals using dilute solutions of the alkali chloride in 1.0 m solutions of $AlCl_3$ in PC; the working reference electrode was a thallium amalgam electrode. The standard potentials of the alkali metals in pure PC were estimated by Jorné, using data from Salomon[74].

As can be seen from Table 1 the choice of solvent has a marked influence on the potential of cation reduction; the trend being toward more cathodic potentials for solvents with higher donor numbers. This is to be expected since the donor number is a measure of the strength of interaction between the solvent and electrophilic species.

The choice of supporting electrolyte has more effect on the kinetics of the reduction than on the thermodynamics. In the case of lithium ions in DMF, varying the cation size of the substituted ammonium perchlorate supporting electrolyte can effect whether the lithium ion is reduced reversibly or irreversibly; the reduction rate constant increases as the crystallographic radius of the supporting electrolyte cation is increased[36]. This behavior is also observed for Na, and K. This effect has been attributed to the influence of the supporting electrolyte cations on the double layer at the cathode[37]. Varying the supporting electrolyte concentration is also reported to have an effect on the lithium reduction potential when tetra-ethyl-ammonium perchlorate (TEAP) is used, although for the larger substituted ammonium cations the supporting electrolyte concentration seems to have little effect. In contrast to what is observed in the study of non-aqueous plating, the identity of the supporting electrolyte anion has not been observed to have a significant effect on the reduction of metal ions at the DME.

In addition to the reduction potential, the standard rate constant of the cation reduction is an indication of the difficulty of reducing a given metal ion. The rate constant is strongly influenced by the experimental environment; Fawcett reports that by varying solvent, supporting electrolyte, and electrode composition, the rate constant for lithium reduction can be varied over eight orders of magnitude[38].

The results of DME studies are not directly transferable to reduction at solid electrodes. Fawcett believed that metal ions were dissolved in the mercury electrode prior to being reduced. If this theory is correct, Fawcett's data reflect a combination of solvent-ion interactions and mercury-ion interactions.[39] Also, systems in which metal cation reduction is relatively facile and chemical reaction with the solvent is minimal are not necessarily the most suitable systems for plating the metal. In addition to allowing the reduction to proceed, the electrolyte system must also be compatible with the presence of a significant quantity of the reduced metal. In some cases, notably lithium in PC, reaction between the metal and the solvent produces a surface film which protects the deposit from further reaction while still allowing the passage of metal ions through the film to the cathode. Because of this, PC is one of the most commonly studied solvents for lithium plating, despite the fact that its relatively high donor number corresponds to greater solvent-ion interaction and therefore lower reduction rate constants and more cathodic reduction potentials than are measured in other aprotic solvents such as tetrahydrofuran (THF) and di-methyl-formamid (DMF). Several attempts have been made to improve lithium cell performance by mixing ethers with PC to raise the electrolyte conductivity by lowering the solution viscosity. These experiments report somewhat higher current efficiencies at the lithium electrode; since most of the ether co-solvents are less reactive with lithium than PC is, the improved efficiency is attributed to less metal loss through reaction with the solvent[40,41]. Amides have also been mixed with PC to lower solution viscosity, but they have a greater reactivity with lithium and the cycling efficiency is consequently lowered[42].

The presence of protective surface films can have a negative effect if the plating process is intended to serve as the charging cycle of a secondary battery. When current is reversed during discharge of the cell, the protective film serves as a barrier to metal dissolution until it is removed from the surface as the metal supporting it is dissolved. Two different overpotentials, corresponding to dissolution through the film followed by dissolution in the absence of the film, have been observed[43]. When the metal is again plated during the charging cycle, some of the metal is lost in forming a new protective film.

By virtue of its position in the periodic table, lithium is the alkali metal which is of the most interest to those looking at the electrochemical behavior of magnesium. Like magnesium its reduction potential is cathodic of the elements in the column below it and, in many cases, its reduction is irreversible. For both metals the difficulty in reducing the cation is often attributed to strong interactions with the solvent, which are in turn attributed to the high charge to size ratio of the cations. In addition to differing in the amount of charge its cation carries, lithium differs from magnesium in having been successfully plated in non-aqueous media. Much research has been performed in improving the quality of non-aqueous lithium deposition; most of it directed toward developing a practical lithium secondary battery. Because of the extensive study of lithium deposition, a brief review of lithium plating research is useful in considering the choices involved in investigating the non-aqueous plating of metals. The extensive literature on the cycling of electrodeposited lithium demonstrates that all of the elements of the electrolytic cell can have a significant impact on the quality of the deposit. Lithium can be plated from many non-aqueous electrolytes with 100% current efficiency[44]; cycling efficiency is lost during the anodic stripping of the deposit[45].

The lower anodic current efficiency is attributed to various interactions between the deposited lithium and the substrate, solvent, lithium salt anion, or any solvent additives or solvent impurities. The charge densities and current densities used can influence the relative significance of these various interactions.

Four criteria are usually used in selecting a solvent: dielectric constant, donor number, viscosity, and chemical stability with the deposited metal. The dielectric constant is used as an indication of how strongly a solvent is likely to dissolve an ionic salt[46]. However, most investigators now rely more on the donor number of a solvent as an indicator of the strength of interaction between the solvent and the solvated cation. As a general rule, it has been observed in ^{13}C-NMR measurements, that when donor numbers of mixed solvents differ by more than 4 units, the solvent with the higher donor number is almost exclusively present in the first solvation shell of the cation[42]. Viscosity of the solvent affects the conductivity of the electrolyte and therefore the power loss due to the IR drop in a plating cell. At the electrodes, lower conductivity may also contribute to raising the overpotential and therefore increasing the likelihood of electrochemical side reactions; including those with the solvent itself. The ease with which a solvent reacts with freshly deposited lithium appears to be less important than the nature of the reaction products. Lithium reacts with all the non-aqueous solvents which are of practical interest for electroplating and only exists for long periods of time as a bulk deposit due to the formation of a protective surface layer, which usually contains decomposition products of the solvent.

The nature of the surface layer is also a function of the solvent purity and the presence of plating additives. Koch and Brummer found that treating PC electrolytes with activated alumina increased the cycling efficiency of the first 5 to 10 cycles, but decreased the total cycling efficiency[47]. The authors concluded that the alumina treatment had removed precursors for the surface layers which favored longer cycling lifetimes. Additives which have been deliberately added to electrolytes in attempts to alter the nature of the surface film include nitromethane, SO_2, and 0.06 M concentrations of water. These additives gave initial improvements in current efficiency, but the improvement was lost after only 10 to 20 cycles[48]. Quinoline dyes have also been reported as effective film precursors[49]; at a fixed current density there is an optimum dye concentration below which the surface film is incomplete and above which the film is too thick and electrodeposition is impeded. When a surface film is allowed to form in the absence of additives there is usually an optimum current density at which there is a balance between metal deposition and protective film formation [50]. Larger charge densities also effect cycling efficiency since surface features, such as dendrites, become more pronounced and lead to greater surface areas for interaction with the solvent. Finally, the anion of the metal salt can be involved in the surface film; in PC solutions the perchlorate anion has been found in lithium surface films and AsF_6^- is reported to form a polymeric surface film with a high density of As-O bonds[51-53].

Nickel and platinum are the two most common substrates used in lithium cycling experiments; neither of them appear to have a significant effect on the character of the deposit. In some experiments aluminum and magnesium have been used as substrates.

Both of these metals alloy with lithium and the lower overpotentials reported for lithium deposition on these substrates are attributed to the free energy of formation of the lithium-substrate alloy[44,55-57]. However, alloy formation leads to the irreversible loss of some of the electroplated lithium, which diffuses into the bulk of the substrate.

B. Reduction and Oxidation Potentials of Magnesium in Non-Aqueous Solvents

Compared with the higher molecular weight alkaline earth metals, the non-aqueous electrochemistry of magnesium has received fairly little attention. In fact magnesium is often omitted from studies of the heavier alkaline earth elements because of anomalous electrode behavior[58]. The work which has been published falls into three general categories: reduction of magnesium ions at dropping mercury electrodes (DME); anodic dissolution of magnesium electrodes; and attempts to reduce magnesium at solid electrodes.

The reduction of Mg^{2+} at dropping mercury electrodes is actually possible in aqueous, as well as non-aqueous, solutions. The ability to form amalgams of alkaline earth metals in aqueous solutions is a consequence of a strong chemical interaction with mercury which is unique to alkali and alkaline earth metals; this interaction leads to reduction potentials in amalgams which are about 1 volt positive of the standard potentials of the metals[59]. Table 4 gives some of the standard potentials which have been measured for magnesium reduction at a dropping mercury electrode[29,30,33,60]. Table 5 contains the half wave potentials for magnesium reduction as measured with respect to the SCE in several solvents[61]. Most of the determinations of the half wave potential were made with tetra-ethyl ammonium perchlorate (TEAP) used as supporting electrolyte. A general trend of increasing half wave potential with increasing solvent donor number is evident. This is to be expected since the donor number is an indication of the strength of interaction between the solvent and an electron deficient species. Table 2 presented the half wave reduction potentials at a DME for several alkali and alkaline earth metals in PC; it should be noted that the magnesium potential is less negative than the potentials measured for the alkali metals, all of which can be plated from PC.

McIntyre and Brown have studied the chemical stability of magnesium amalgams in PC, DMF, and Acetonitrile (AN)[29]. The potential of a streaming amalgam electrode containing 10^{-3} weight fraction magnesium was compared with the potential of a stagnant pool of the amalgam. In PC and AN the potentials of the pool electrodes were approximately 200 mV less cathodic than the streaming electrode potentials. In DMF there was no significant difference in potential between the two electrode configurations. The authors attributed the difference in potential in the presence of PC and AN to the consumption of magnesium in the pool electrodes by reaction with the solvent.

Louati and Gross studied the reduction of complexed and uncomplexed magnesium ions at a DME[61]. The uncomplexed system consisted of $Mg(ClO_4)_2$ in PC with tetra-isopentyl ammonium iodide as the supporting electrolyte. The half wave potential of -1.62 volts versus the SCE was found to be independent of the magnesium

Table 4. Half Wave Reduction Potentials of Magnesium at a Dropping Mercury Electrode

E½	Reference Electrode	Solvent	DN	Supporting Electrolyte	
-1.72	SCE	PC	15.1	TEAP	1
-1.940	Ag/AgCl	water	33	$MgCl_2$	2
-1.980	Ag/Ag^+	water	33		3
-2.255	$Ag/AgNO_3$	AN	14.1	$Mg(ClO_4)_2$	3
-2.110	$Ag/AgClO_4$	PC	15.1	$Mg(ClO_4)_2$	3
-2.468	$Ag/AgNO_3$	DMF	26.6	$Mg(ClO_4)_2$	3
-2.30	SCE	DMA	27.8	TEAP	4

1 Gutman,Kogelnig,Michlmayr,Monatscheft fur Chemie,99,693(1968)
2 Longhi,Mussini,Osimoni,La Chimica e L'Industria,55(1),888(1973)
3 Brown,McIntyre,Electrochimica Acta,29(7),995(1984)
4 Gutman,Michlmayr,Peychal-Heiling,J. Electroanal. Chem.,17,153(1968)

Table 5. Half Wave Potentials for Magnesium Reduction at a Dropping Mercury Electrode (Volts cathodic of SCE)

Solvent	DN	Supporting Electrolyte	E½
acetic anhydride	10.5	TEAP*	1.06
benzonitrile	11.9	TEAP	1.62
acetonitrile	14.1	$NaClO_4$	1.84
PC	15.1	TEAP	1.72
Isobutyronitrile	15.4	TEAP	1.68
propionitrile	16.1	TEAP	1.72
N-N-DMA	27.8	TEAP	2.30
DMSO	29.8	$TEA(NO_3)$	2.28
water	33	TEAI	2.2

* tetra-ethyl-ammonium perchlorate
Louati,Gross,Electrochimica Acta,21,7(1976)

concentration. The bicyclic diamine, cryptate, was used to complex magnesium. The supporting electrolyte in this system was tetra-heptyl ammonium chloride. The half wave potential in the complexed solution varied from -2.15 to -2.38 volts as the magnesium complex concentration was varied between 4 x 10^{-4} M and 1.025 x 10^{-3} M. However, the rate constant was faster in the complexed solution (2.3 x 10^{-3} cm/sec versus 1.45 x 10^{-4} cm/sec). This is in contrast to sodium and potassium, which are reduced much faster in the absence of the cryptate ligand. Evidently it is more difficult to de-solvate Mg^{2+} from PC than to remove it from the ligand. This strong interaction with the solvent is one of the difficulties encountered in attempting to plate magnesium. In DMSO, with a donor number of 29.8 (the donor number in PC is only 15.1), the interaction with the solvent is so strong that the rate constant for Mg^{2+} (as well as Ca^{2+} and Sr^{2+}) reduction at a DME is too small to be measurable[62].

The use of magnesium as an anode in non-aqueous electrolytes was studied by Saito et. al.[63]. The results of polarization experiments in several solvents are reproduced in Table 6. The potentials reported were measured with respect to the SCE and represent steady state values after three minutes of current. With the exception of the electrodes in formamide(FA), a black film formed on the magnesium anode in all of the solvents. This film was removed at higher current densities. The supporting electrolytes in these experiments were either sodium or lithium perchlorate. In the present study I found that a magnesium anode in 1.0 m $Mg(ClO_4)_2$ in PC was free of the black film observed by Saito when $LiClO_4$ was used. The effect of the film on the

Table 6. Potentials of Magnesium Anodes in Non-Aqueous Solvents
(Potentials cathodic of SCE)

	Current (mA/cm^2)				
Solvent	0	0.05	0.10	1.00	10.0
PC^1	1.21	0.26	0.24	0.09	
THF^1	1.18	0.45	0.44	0.36	
DME*^{2}	1.19	0.60	0.59	0.54	0.35
AN^2	1.09	0.72	0.70	0.65	0.62
FA^2	1.40	1.38	1.25	1.05	0.63
(1:1)^a					
PC-THF^1	1.14	0.25	0.23	-1.6	
PC-DME^1	1.14	0.49	0.47	0.30	1.5
FA-DME^2	1.45	1.30	1.22	0.77	0.40
FA-THF^2	1.44	1.25	1.15	1.02	0.59
FA-AN^2	1.47	1.46	1.45	1.37	0.47

* 1,2 dimethoxyethane
a 1 to 1 volume mixtures
1 1 M $LiClO_4$
2 1 M $NaClO_4$

Saito,Ikeda,Matsuda,Tamura,J. Appl. Electrochem.,6,85(1976) electrode potential is evident in Table 6; in the film free formamide solutions, the anodic overpotential is lower. In mixed solvents, the presence of FA appears to dominate the electrode behavior. Brown and McIntyre studied the electrodissolution of magnesium in DMF, AN, and PC[64]. In tetra-ethylammonium perchlorate solutions, dissolved oxygen in the electrolyte hindered the dissolution of magnesium, while water concentrations of 0.1 volume percent had no effect on the dissolution. The rate constant for magnesium electrodissolution was estimated to be on the order of 10^{-8} cm/sec. Large overpotentials were required before anodic dissolution of solid magnesium electrodes occurred; this behavior was attributed to the native oxide film on the metal surface. After electrodissolution, the electrode surface again became covered with a film. This second film appeared to be different from the initial surface film.

Peled and Straze[65] claimed to have deposited magnesium onto a nickel substrate from a solution of $Mg(FeCl_4)_2$ in thionyl chloride. The identification of the deposit was made by comparing the potential of the deposit with a magnesium wire immersed in the electrolyte. Since Peled observed that magnesium in thionyl chloride is always covered by a surface film, it is likely that the cathodic deposit on the nickel electrode was the same material formed by the reaction of magnesium with thionyl chloride. I have found that the potentials of cathodic deposits from $Mg(BF_4)_2$ solutions in PC are very close to the potentials of magnesium rods in the same electrolyte, even though the cathodic deposits are only 10% magnesium. In Peled's experiments, the deposit on the nickel cathode was produced by a 150 $\mu A/cm^2$ current applied for one hour; during this time the cathodic overpotential rose to -20 volts with respect to a magnesium wire reference. When the current was stopped the cathode potential dropped to within 30 mV of the magnesium reference; this was the basis for identifying the deposit as magnesium. The deposit is believed to have dissolved soon after the current was stopped, since the potential rose to 1.8 volts, which is the potential of nickel in the thionyl chloride electrolyte.

IV. Propylene Carbonate

Most of the experiments in this investigation were performed using propylene carbonate (PC) based electrolytes. PC has many properties which make it an attractive, non-aqueous electrolyte for metal deposition: it is stable over a wider potential range than water, it is aprotic, and with a dielectric constant of 65 it is an effective solvent for many ionic salts. PC is also liquid between -49°C and 241°C, has a very low vapor pressure, is non-toxic, and is not flammable. These last properties make PC preferable to ethers for use in commercial electrochemical cells. All of the alkali metals have been electrodeposited from PC based electrolytes.

The actual potential range over which PC is stable varies with the electrode material used and the degree of purity of the solvent. On platinum electrodes PC is reported to be stable between -1.76 and 1.94 volts versus SHE, while on mercury the potential range is -2.70 to 0.64 volts[4,61]. On graphite electrodes PC is reduced at -2.40 volts versus SHE[51]. Eidinger studied the cathodic reduction of PC solutions of potassium and lithium salts at several electrode materials[66]. The primary reaction products were propene gas and carbonate, although some reaction of the solvent with electro-reduced alkali metal was also suspected. The solvent was actually found to decompose anodic of the metal deposition, but at much lower current densities than are attainable in metal deposition. Once the electrode is covered with the alkali metal, cathodic reduction of the solvent is replaced by chemical reaction with the alkali metal to form a protective surface film: this film is composed of metal alkyl carbonates.[51,52]. When higher surface area electrodes, such as metal felts, are used as cathodes, significant decomposition currents are observed at less cathodic potentials than at smooth electrode surfaces.

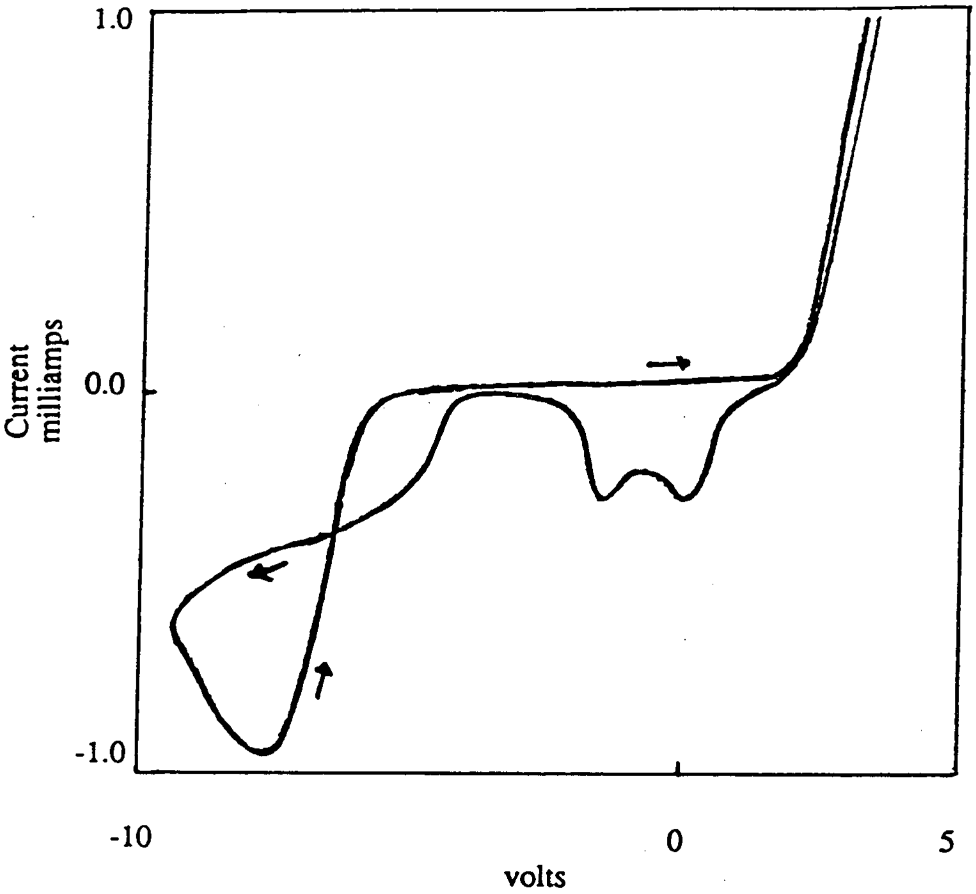
Cyclic voltammetry was performed using several of the PC based electrolytes used in this investigation. These experiments failed in their initial goal of determining a reduction potential for magnesium, but provided information on the electrochemical stability of the electrolytes. The cell used in these experiments was the same one used by Hanson[35] in the study of iodine salts in PC. The working electrode was a platinum disc with a surface area of about 0.14 cm^2. A platinum wire embedded in the bottom of the cell served as a counter electrode. A thallium halide/thallium amalgam reference electrode was used (see the experimental part of the discussion of $AlCl_3$ electrolytes for details of the reference electrode). TlBr was used as the halide salt with 0.75 m tetra-propyl ammonium bromide as the supporting electrolyte in the reference cell. Cyclic voltammograms were performed with and without supporting electrolyte in the working cell. The potential was controlled using a PAR 173 potentiostat with a PAR 175 universal programmer. Voltammograms were recorded using a Nicolet 1090A digital oscilloscope interfaced with a HP 9825 desktop computer.

Cyclic voltammetry of the supporting electrolyte at a scan rate of 200 mV/sec showed that cathodic decomposition of the electrolyte started at -1.76 volts with respect to the TlBr/Tl(Hg) reference. Anodic decomposition currents were observed at 1.50 volts. Bromine ion oxidation appears to overlap the oxidation of the solvent. Hanson was able to study the oxidation of complex iodine anions in PC, but attempts to perform similar studies with bromine species were unsuccessful due to the overlap with the solvent oxidation[35]. Bromine oxidation can be inferred from the appearance of cathodic peaks at 0.69 and 0.21 volts on the cathodic return sweep. When 0.1 molal $MgBr_2$ was added to the supporting electrolyte, there was no discernible change in the voltammogram.

Cyclic voltammetry was performed on 1.0 m solutions of $AlCl_3$, mixtures of 0.1 $MgBr_2$ and $AlCl_3$, and the products of attempts to form a double salt by fusing the two chemicals. The cathodic ramps in these experiments were extended to -10 volts, at a cycling speed of 200 mV/sec. An electrolyte reduction current started at about the same potential as was observed in the tetra-propylammonium bromide solution, but at about -5 volts the current stopped rising and formed a plateau, which extended to -9.5 volts. At -9.5 volts the current rose dramatically. On the anodic return scan, the current at potentials cathodic of -4 volts was often higher than on the cathodic scan. This behavior is illustrated in Figure 1, which is a cyclic voltammagram of a 1.0 m solution of $AlCl_3$ in PC. When the scan rate was reduced to 2 mV/sec the plateau started at -3.5 volts and a distinct peak was observed at the leading edge of the plateau. This current plateau represents the formation of a film on the electrode, which slows the rate of solution reduction. At -9.5 volts sufficient current is passed through the film for rapid electrolyte reduction to resume. When the potential ramp was cycled, the observed current decreased with each successive cycle; this behavior is consistent with continuing film growth on the electrode. Replacing the electrode with a fresh platinum disc resulted in currents of the same magnitude as the first scan on the original electrode, proving that the decrease in current was not caused by the reduction

Figure 1. Cyclic Voltammogram of 1.0 m $AlCl_3$ in PC

200 mV/sec. Scan Rate



Potential with respect to TlCl|Tl(Hg) reference electrode of dilute impurities in the solution, but by the loss of electrode activity. Allowing used electrodes to sit for an hour between cycling experiments also resulted in a substantial recovery of electrode activity. In galvanostatic experiments using $AlCl_3$ solutions (described in a later section of this report), surface films became visible on aluminum cathodes after the passage of 1 or 2 coulombs/cm^2. When the current was stopped at this point, the films dissolved back into solution; this accounts for the recovery of electrode activity when the electrode is allowed to rest between cyclic voltammetry experiments. The cathodic branches of cyclic voltammograms of solutions containing $MgBr_2$ in addition to 1.0 m $AlCl_3$ contained no features which could be attributed to the reduction of the Mg^{2+} ion.

When solutions containing chlorine species were cycled anodically, peaks were observed at approximately 5.5 and 6.5 volts, followed by a large oxidation current at 9 volts. The extremely anodic potentials of the two peaks indicates that they involve an anodic surface film. On the cathodic return sweep from the anodic voltages, two reduction peaks appeared at potentials between 1 and -1 volts. These two peaks are visible in Figure 1. The observed variation of these reduction peak potentials with repeated cycling is probably a result of the changing character of the electrode surface as the film grows.

V. Magnesium Tetrafluoroborate Electrolytes

A. Magnesium Tetrafluoroborate in Propylene Carbonate

Flouroborate salts are often used in non-aqueous electrochemistry because of their stability and the high solubility of the large anion. Magnesium tetrafluoroborate was also selected for study on the basis of several previous studies which had indicated that boron containing species might have a beneficial effect on the reduction of magnesium cations. In Brenner's 1971 report of magnesium deposition from an ether based bath, an unidentified magnesium/boron species was formed from a reaction between $LiAlH_4$, $MgCl_2$, and decaborane[25]. Both Brenner and Jorné report possible magnesium deposits from solutions of $MgBH_4$ in diethyl ether or propylene carbonate(PC)[4,23]. Jorné's work also raised the possibility of metallic deposits from $Mg(BF_4)_2$ solutions in PC. Gregory et. al. report high purity magnesium deposits from solutions of magnesium bis-organoborate compounds, $Mg(BR_4)_2$, in tetrahydrofuran[26].

Synthesis

Unlike the alkali metals and the higher molecular weight alkaline earths, the reaction of magnesium fluoride and boron trifluoride to form the fluoroborate salt is endothermic, with a heat of formation of 39 kcal/mole. In this respect magnesium behaves more like a transition metal than an alkaline earth metal[67]. Because of this high heat of formation, $Mg(BF_4)_2$ can only be formed in strongly coordinating solvents in which the heat of solution can compensate for the heat of formation. Jorné synthesized $Mg(BF_4)_2$ by bubbling BF_3 gas through an agitated slurry of insoluble MgF_2 in PC. This synthesis is fairly difficult due to the corrosive nature of BF_3 gas and some solvent decomposition occurs during the reaction. However, this technique does offer the advantage of avoiding contact of the magnesium salt with water. Jorné also produced $Mg(BF_4)_2$ through the aqueous substitution reaction:

$$Mg(ClO_4)_2 + 2KBF_4 \rightarrow Mg(BF_4)_2 + 2KClO_4$$

which is driven forward by the precipitation of the insoluble potassium perchlorate. After several hours, Jorné chilled the solution to further reduce the potassium perchlorate solubility and filtered the solution. This synthesis had two drawbacks: the magnesium salt had to be thoroughly dried to avoid contaminating electrolytes with water and potassium could not be completely removed from the product by the solubility difference. This second problem was especially damaging. Because potassium is much easier to reduce than magnesium is, even a fairly low concentration of potassium in a $Mg(BF_4)_2$ solution results in a cathodic deposit which is almost completely composed of potassium.

In the present work an attempt was made to improve the purity of the $Mg(BF_4)_2$ produced from the aqueous substitution reaction by dissolving the dried product in acetone, which should selectively dissolve fluoroborate salts. The acetone solution was chilled and filtered, but it proved difficult to distill the acetone off of the salt. At room temperature the house vacuum was too weak to remove the acetone and at higher temperatures a thick red gel formed in the still pot; apparently $Mg(BF_4)_2$ polymerizes the acetone. On a vacuum line at a pressure of 1 or 2 Torr, acetone removal was hindered by the formation of a surface film on the acetone solution. Shaking the solution broke the film, but the dried product was severely discolored. This method of $Mg(BF_4)_2$ synthesis was not pursued further.

To avoid contaminating $Mg(BF_4)_2$ with other metal ions, synthesis was attempted using fluoroboric acid (HBF_4). All syntheses using HBF_4 were performed in the glove box under a He atmosphere. Fluoroboric acid (Fluka) was purchased as a 54 wt. % solution in diethyl ether and stored over a mixture of 3 and 4 Å molecular sieves to remove trace water from the solution. Magnesium filings were added to the fluoroboric acid solution in an attempt to directly produce the salt from the metal and the acid, but no reaction was observed after a weak of agitation. Synthesis was then attempted using $MgCl_2$ as the magnesium source:

$$MgCl_2 + 2HBF_4 \rightarrow Mg(BF_4)_2 + 2HCl$$

This synthesis introduces no foreign metal ions to the product and the gaseous byproduct is easily removed. Measuring the final chlorine concentration is an easy way of evaluating the extent of reaction. Also, unreacted $MgCl_2$ would have little effect on the use of the product in electrolyte preparation, since it is virtually insoluble in PC. The chief drawback to this synthesis is the possibility of introducing hydrogen into the aprotic solution in the form of unreacted acid.

The reaction was first attempted in PC solution in the belief that the solubility of the product $Mg(BF_4)_2$ would drive the reaction forward. Stoichiometric amounts of the salt and the acid were mixed in a r.b. flask and sufficient PC was added to form a 0.5 m solution if the reaction went to completion. Prior to the addition of the PC some gas evolution was observed. Addition of PC produced a milky suspension. When stirring was stopped a sediment collected on the bottom of the flask. After one week of stirring the reaction mixture was light brown. Elemental analysis of the filtered PC proved that no reaction had occurred since magnesium was only present at a millimolal concentration.

Synthesis was next attempted without using PC. The ethereal acid solution was placed in a r.b. flask with a magnetic stir bar. Sufficient $MgCl_2$ to react 44% of the acid was slowly added to the solution. The reaction vessel was left uncovered to allow HCl gas to bubble away from the reaction. The $MgCl_2$ appeared to be insoluble in the ether solution. After 6 days of stirring the only visible change in the reaction mixture was a darkening of the solution. The ether was allowed to evaporate from the vessel and the residual solid was submitted for elemental analysis. Elemental analysis was performed by the Microanalytical Laboratory at the U.C. Berkeley College of Chemistry. The product solid was found to be virtually free of chlorine. On a reactants only basis (neglecting the weight of the ether), chlorine had dropped from an initial weight percentage of 14.4% to a final value of 0.09%. Magnesium concentration rose from 4.9% to 8.0%. This magnesium concentration is actually higher than that of pure $Mg(BF_4)_2$ and is probably an artifact of the sample preparation for elemental analysis. The solid product was hygroscopic and was dried by the analytical laboratory to remove absorbed atmospheric water. This drying probably caused some thermal decomposition of $Mg(BF_4)_2$ to MgF_2 and BF_3. The product was found to be almost completely soluble in PC, with only a small amount of white sediment failing to go into solution. This sediment was attributed to unreacted $MgCl_2$.

The above synthesis was repeated using more vigorous stirring. Upon adding $MgCl_2$ to the agitated acid solution, gas began to evolve rapidly enough to form a froth over the solution. Since $MgCl_2$ should have much less effect on a PC plating bath than fluoroboric acid, sufficient $MgCl_2$ was added to react all of the acid present. Over the course of two days the solution thickened and eventually formed a solid as the ether was allowed to evaporate. The product was a very light brown, porous solid which was not hygroscopic. Elemental analysis showed that chlorine had dropped from 31.4% of the reactant weight to 0.7% of the product weight. Based on elemental analysis, the product is believed to have been over 90 percent $Mg(BF_4)_2$ with traces of unreacted $MgCl_2$ and entrapped ether.

$Mg(BF_4)_2$ was also obtained by drying a commercially available 30 wt. % aqueous solution(Alfa). The drying was performed on a vacuum line capable of attaining vacuums of one to two Torr. Water was collected in cold traps immersed in liquid nitrogen. The temperature of the fluoroborate solution was kept between 80 and 100°C. At higher temperatures the tetrafluoroborate salt decomposes to form a white solid, which is insoluble in PC, and a gas which attacks the glass walls of the vacuum line. Analysis of the corroded glassware showed that fluosilicic acid had been formed. Based on this behavior, and by analogy with $LiBF_4$ decomposition[68], the products are believed to be MgF_2 solid and BF_3 gas. Even when the still pot temperature is maintained below 100°C, a small amount of decomposition is evident. Because of this decomposition, the percentage of magnesium in the dried salt is always slightly higher than it would be in pure $Mg(BF_4)_2$ and there is always a small fraction of the sample which is insoluble in PC. Overall this is preferable to a product in which the magnesium content is lower than in pure $Mg(BF_4)_2$, which would indicate a substantial amount of water of hydration in the product.

Electrolyte Preparation

PC was cooled to almost 0°C on a cold plate in the glove box. $Mg(BF_4)_2$ was added slowly in small amounts. After each addition the salt was allowed to completely dissolve before further additions were made. When dissolution was complete, 3 and 4 Å molecular sieves were added to the solution. After 24 hours a fresh charge of molecular sieves was added and the solution was allowed to sit for a further 24 hours. Inorganic salt solutions in PC have final water concentrations of about 1 ppm when treated with molecular sieves in this manner[69]. This concentration refers only to free water in the solvent. Any trace water which is intimately involved in the primary solvation shell of the ions would not necessarily be removed and would escape detection by analysis using gas chromatography, infrared spectroscopy, or NMR. Prior to use, the solutions were filtered through Whattman GF/F glass fiber filters to remove the molecular sieves and insoluble impurities.

Solutions ranging in composition from 0.5 to 1.0 molal were used in the various electrolysis experiments. Over this concentration range there was no discernable variation in the electrode reactions.

Experimental

Three different cells were used in electrolysis of $Mg(BF_4)_2$ solutions: an H cell with 2.5 cm diameter legs and a 7 cm long, 1 cm diameter crosspiece with a glass frit between them; a smaller H cell with 2 cm diameter legs and no frit between them; and a single chamber cell used in some of the magnesium electro-polishing experiments and in micropolarization experiments. The smaller H cell was fitted with teflon electrode holders which kept the metal rod electrodes used in the experiments centered in the cell chambers. The micropolarization experiments were performed in a 2.5 cm diameter cell fitted with teflon electrode supports which kept 1 cm^2 metal foil electrodes spaced 1 cm apart. The electrode supports were designed with sufficient clearance beneath the electrodes to allow the electrolyte to be magnetically stirred. The spacing pieces which kept the electrodes 1 cm apart were notched to allow the teflon lead of the amalgam reference electrodes to be held flush with the working electrode surface. Platinum foil electrodes were soaked in nitric acid, rinsed in de-ionized, distilled water, and dried under vacuum before being transferred to the glove box. Magnesium anodes were treated in the same way. All electrolysis experiments were performed under He atmosphere in a glove box.

Cathodic Deposition Experiments

Cathodic deposition was first attempted using the larger H cell with the glass frit between the anodic and cathodic chambers. A 2 cm^2 platinum foil was used as the cathode and a magnesium rod with a surface area of 3.14 cm^2 was used as the anode. The electrolyte was 0.7 m $Mg(BF_4)_2$ with a conductivity of 2.9 x 10^{-3} siemens/cm. 53 coulombs were passed through the cell at an anodic current density of 0.5 mA/cm^2 and a cell potential drop of 2.2 volts. Gas evolution was observed at the cathode during polarization. With the exception of a few black dots on the platinum surface the cathode was unchanged. The experiment was then repeated at higher current density using a fresh charge of electrolyte and new electrodes. 1760 coulombs were passed through the cell at a cathodic current density of 5 mA/cm^2. During the course of the experiment the potential drop rose from 24 to 75 V and gas evolved at the cathode. Later experiments with reference electrodes placed near the cathode showed that almost all of this potential rise was due to resistance in a growing deposit at the cathode. Immediately after the electrolysis the cathode was coated with a thick black film. After drying in the He atmosphere of the glovebox, the film was bright white. This coating was 33 wt. % magnesium and approximately 1.5 wt. % each of carbon and hydrogen. Boron made up about a quarter of a percent of the deposit weight.

To reduce the amount of electrolyte needed in the experiments, subsequent experiments were performed in the smaller H cells. In these cells the anodes were magnesium rods and aluminum rods were used as cathodes. The aluminum rods were cleaned with organic solvents, rinsed with deionized, distilled water, and dried under vacuum prior to use. Aluminum was selected as a cathode material based on lithium plating experiments in which the deposition overpotential was lower on aluminum than on platinum. The decrease in overpotential was attributed to alloy formation between the metals[44,55-57]. Comparisons were made between aluminum used with the native oxide and aluminum which had been thoroughly filed in the glovebox. Although deposits formed quicker on the filed surfaces, the final compositions of the deposits did not appear to be influenced by the initial state of the substrate.

$Mg(BF_4)_2$ solutions made with the fluoroboric acid synthesis were compared with solutions made with the dried aqueous $Mg(BF_4)_2$. No difference in cathodic behavior could be found between solutions from these sources. Since the synthesis using $MgCl_2$, and fluoroboric acid results in a product which is contaminated with $MgCl_2$, HBF_4, and di-ethyl ether, most of the electrolytes were prepared using the vacuum dried $Mg(BF_4)_2$ from the aqueous source.

A series of experiments was performed to examine the effect of current density and quantity of charge passed on the nature of the cathodic product. These experiments were performed in the small undivided H cells, using a stock solution of 0.75 m $Mg(BF_4)_2$, aluminum rod cathodes with filed surfaces, and magnesium rod anodes. The conductivity of the $Mg(BF_4)_2$ solution was 1.90×10^{-3} siemens/cm. During electrolysis the catholyte was continuously stirred. The weight percent of magnesium in the cathodic deposits was determined by Atomic Absorption Spectroscopy. Some of the deposits were also analyzed for boron content to determine if the BF_4^- anion was involved in the cathodic reaction. Regardless of the conditions used in each experiment, boron comprised a fairly consistent 2.5% of each deposit. All deposits were rinsed with PC prior to analysis.

Three distinct regions of cathodic behavior were observed. These regions can be correlated with the applied current density. Below 0.8 mA/cm^2 small black spots form on the cathode surface; these spots contain less than 5 wt. % magnesium. Charges of 2.5, 68, and 159 coulombs were passed through the cell in this current density range. As the quantity of charge was increased, the ratio of magnesium content in the cathodic product to the total charge passed decreased. The deposit weight was also fairly insensitive to increasing the charge passed. A possible explanation of this behavior involves the reduction of magnesium at certain active sites on the cathode, followed by re-oxidation of the magnesium atoms by reaction with solvent molecules. Once the magnesium is oxidized, the site loses its electrical activity and solvent decomposition with accompanying gas evolution is the dominant electrode reaction. In this current density range the potential drop across the cell varies between 2 and 3 volts. At current densities of 0.8 to 1.0 mA/cm^2, a uniform, shiny, black deposit coats the cathode. This deposit is about 20 wt. % magnesium. Tripling the charge passed from 51 to 179 coulombs only increases the deposit weight by 33%. As was noted in the lower current density region, the reactions which produce the cathodic deposit become less significant as the electrode is covered and gas evolution becomes the major cathodic reaction. The potential drop across the cell varied between 3 and 5 volts in this current density range. Throughout the course of these experiments the potential drop increased steadily with time. This increase is attributed to the resistance of the growing cathodic deposit. At current densities between 5 and 25 mA/cm^2, the cathode is coated with a thick, grey, porous deposit which is only about 10 wt. % magnesium.

Gas evolution was vigorous at these current densities and may account for the porous nature of the electrode product. Cell potential drops varied between 25 volts at 5 mA/cm^2 and 85 volts at 25 mA/cm^2. Although the deposits formed at 5 and 25 mA/cm^2 looked similar, it is believed that a larger fraction of the current was involved in gas evolution at the higher current density. When 180 coulombs were passed at each current density, the deposit formed at 5 mA/cm^2 was three times heavier than that formed at 25 mA/cm^2.

In some cases it appears that the re-oxidation of magnesium at the cathode may be the dominant cell reaction. Since the anodic dissolution of magnesium was found to be much more facile than the cathodic reduction process, experiments were often performed with larger cathodes than anodes to allow larger net currents to be passed across the cells. This results in experiments in which a relatively large amount of the cathodic reduction product is exposed to the electrolyte. In one such experiment the cathode was 7.2 cm^2 and the anode was .375 cm^2. A current of 0.25 mA was passed between the electrodes. Initially the potential drop was 20 volts, but within 10 minutes the magnitude had decreased to only 11 volts. Over the next 90 minutes the potential drop decreased at a slower rate, but eventually reversed polarity to 0.47 volts with the nominal cathode anodic of the magnesium anode. Doubling the current to 0.50 mA restored the initial cell polarity. The gradual change in polarity may be a consequence of chemical oxidation of electrically reduced magnesium; doubling the current restored net reduction at the cathode and therefore maintained the original cell polarity.

The grey porous deposit formed at high current densities is not just a more massive version of the black coating formed at 1 mA/cm^2. This was proven by maintaining a current density of 1 mA/cm^2 till the cathode was completely covered. When the current density was raised to 3 mA/cm^2, the black coating disappeared and was gradually replaced by the grey coating. None of the deposits produced at current densities greater than 5 mA/cm^2 resulted in the white deposit observed at 5 mA/cm^2 in the divided H cell. In that experiment a total charge of 1760 coulombs was passed, as opposed to only 180 coulombs in the second set of experiments. The difference in deposit character is attributed to a temperature effect resulting from IR heating of the electrolyte in the longer experiment. This conclusion is supported by a later experiment in which the cell was heated during electrolysis.

Several attempts were made to reduce the overpotential for magnesium reduction by altering the cathode surface with an electrodeposited sodium/magnesium alloy. Jorné reported that an alloy of sodium and magnesium could be obtained from a PC solution of $NaBF_4$ and $Mg(ClO_4)_2$[4]. In the present experiment a solution of 0.2 m $NaBF_4$ and 0.1 m $Mg(ClO_4)_2$ in PC was used in preparing the alloy. At higher concentrations of $NaBF_4$ the sodium salt was not completely dissolved. At a current density of 1 mA/cm^2 a deposit containing 8 times as much sodium as magnesium was produced. A 3.6 coulomb charge of this alloy was plated onto an aluminum rod, followed by 157 coulombs in 0.5 m $Mg(BF_4)_2$ in PC. The potential drop across the cell was 4 volts for the second plating. The final deposit had.roughly equal amounts of sodium and magnesium, although the metals made up only 20 percent of the deposit weight. In a second experiment an alloy charge of only 0.9 coulombs was followed by 130 coulombs in the $Mg(BF_4)_2$ plating bath. During the second plating the potential drop across the cell was 10 volts. The final magnesium content was over four times higher than the sodium content, although the total metals weight was still only 20 percent of the deposit. In both experiments the alloy pre-deposition was light grey and porous. After the second plating the surface was smooth and black. Assuming that the alloy layer had contained eight times as much sodium as magnesium, the concentration of magnesium in the the second layer can be calculated as 17 wt. % in both of the previous experiments. When a bare aluminum rod was used at the same conditions, the magnesium content was only 11 wt. %. The use of an alloy pre-deposition therefore results in a measurable, but practically insignificant improvement in the quality of the cathodic deposit.

When PC solutions of $LiAsF_6$ are used in lithium plating experiments, a protective surface film is formed which contains a substantial number of As-O bonds[29]. The anionic decomposition product, AsF_3, is reported to be an important precursor in the formation of the protective film. An attempt was made to form an analogous surface film in a magnesium electrolyte. The first approach to forming such a system involved adding liquid AsF_3 to an agitated slurry of MgF_2 in PC in an attempt to form a soluble magnesium salt. This reaction scheme is analogous to the formation of $Mg(BF_4)_2$ in PC by reacting MgF_2 in PC with BF_3 gas; reaction progress is monitored by the consumption of the insoluble MgF_2. Jorné successfully used this reaction scheme[4]. However, no reaction was observed between MgF_2 and AsF_3. A second attempt to produce an As-O protective surface film was made by adding drops of AsF_3, a film precursor, directly to a 0.5 m solution of $Mg(BF_4)_2$ in PC. The cathode used in this experiment was an aluminum rod with a magnesium/sodium electrodeposit on the surface. Both the pre-plating and the $Mg(BF_4)_2$ plating were performed at 0.15 mA/cm^2. The voltage drop across the cell averaged about 4 volts during the pretreatment of the cathode. During the $Mg(BF_4)_2$ plating the voltage drop was initially only about 1.5 volts. When 3 to 4 drops of AsF_3 were added to the electrolyte the voltage quickly rose to 4 volts and then gradually returned to 2.5 volts. The voltage then continued to rise and fall over a 3 volt range in cycles with life times of about half an hour. During the course of the experiment the average value of the voltage drop rose steadily. By the time 15 coulombs had been passed through the cell, the potential drop was cycling between 3.5 and 6.5 volts. The resulting deposit was black and smooth. Analysis of the deposit did not show any dramatic improvement in magnesium content over experiments performed without the AsF_3 additive. AsF_3 did have the negative effect of forming a precipitate with $Mg(BF_4)_2$ and apparently also attacked the pre-plating. After electrolysis of 25 ml of .5m $Mg(BF_4)_2$ with 10 drops of added AsF_3, elemental analysis showed that the electrolyte was only 0.23 m in magnesium, .004 m in sodium, and 1.197 m in fluorine. The precipitate included a substantial amount of the organic solvent; elemental analysis of the dried precipitate gave weight percentages of only 0.65 % magnesium, 0.10 % sodium, 0.51 % boron, 2.4 % fluorine, and 1 % arsenic. The cycling of the potential drop was probably due to changes in electrolyte conductivity as the concentration of $Mg(BF_4)_2$ was altered by the presence of AsF_3. The potential variation may also have been influenced by differing cathodic reactions in the presence of AsF_3, which would have been depleted as the precipitate formed. No further experiments were made using AsF_3.

Anodic behavior of Magnesium in $Mg(BF_4)_2$ solutions in PC

Magnesium rods have been successfully electropolished in $Mg(BF_4)_2$ solutions with 100% current efficiency. Above a certain minimum value, the magnitude of the anodic current density is less important than the uniformity of the current density. During magnesium electrodissolution two surface films are formed. At regions of low current density, such as the face of a magnesium rod furthest from the cathode, a thin black film forms. At regions of higher current density a gelatinous, yellow film forms. The yellow film is easily wiped off the anode, revealing the electropolished surface. Electropolishing has only been observed under this yellow film. When sufficient charge is passed the yellow film grows under the black film. In some experiments a cylindrical cathode was placed around a central magnesium rod anode to assure a uniform anodic current density; in these experiments the black film was not observed. Even when the magnesium surface was mechanically roughened prior to electrolysis, the final surface had a mirror finish; only the end face of the rod, where the current density was lower than on the vertical face, remained rough. Successful electropolishing was performed at current densities varying between 5 and 40 mA/cm^2.

Both current distribution and charge density seem to be important variables in the successful electropolishing of magnesium. In experiments in which the current density was not uniform, the black film formed before the yellow film was observed. If current was stopped prior to the appearance of the yellow film, the black film could only be partially removed and the underlying magnesium surface was rough. The anodic current efficiency of these experiments was only about 90%. Successful electropolishing appears to require sufficient magnesium dissolution to isolate the magnesium substrate from the black surface layer. Current densities of 1 mA/cm^2 and minimum charge densities of 200 coulombs/cm^2 appear to be sufficient to ensure that the black film is isolated from the metal surface.

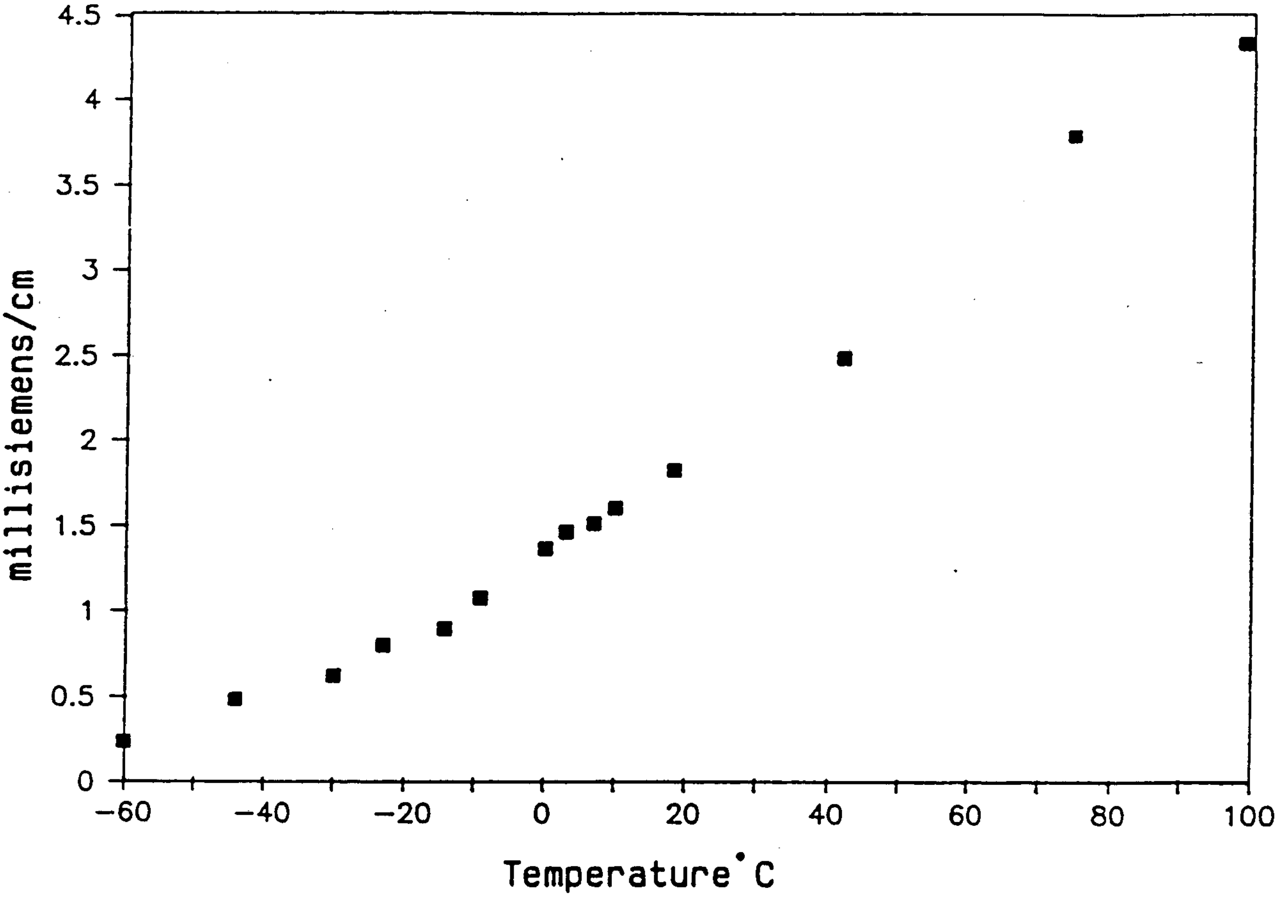
Two questions have not been satisfactorily answered at present: is the yellow layer absolutely necessary for electropolishing and are the precursors of the yellow film formed at the cathode. Two experiments were performed in which an H cell with a glass frit between the chambers was used. The far side of the magnesium anodes were coated with Kynar insulator to leave an active area with a more uniform current density. When charges of 200 coulombs/cm^2 were passed at 5 mA/cm^2, the black film was observed at the edges of the active area and both the yellow film and electropolishing were absent. However, when 1760 coulombs were passed in the same cell without insulator on the far side of the anode, the surface was clean and electropolished at the end of the experiment, although during the course of the experiment yellowing of the anode had been observed. The lack of a yellow layer at the end of this experiment may be a consequence of two possible effects: vigorous bubbling at the anode may have dislodged the layer or IR heating of the solution over 4 days of electrolysis may have heated the solution sufficiently to dissolve the layer. In an experiment in an undivided cell which had been heated to 100°C, the yellow layer was also absent. Further experiments are needed to clarify the origin and effect of the yellow layer.

An attempt was also made to measure the exchange current density of magnesium in $Mg(BF_4)_2$. The cell used in these experiments was the small single chamber cell with foil electrodes described above in the experimental section. The reference electrode used was a TlCl|Tl(Hg) reference electrode with 0.7 m $Mg(BF_4)_2$ as the electrolyte. The complete cell with reference electrode and the magnesium foil electrodes was allowed to equilibrate for 24 hours before micropolarization experiments were attempted. These experiments were unsuccessful due to the reactivity of the magnesium surface in contact with the electrolyte. Initially the magnesium surface was about 0.65 volts cathodic of the reference electrode, but this value was unstable and oscillated over a tenth of a volt over the duration of an hour. Attempts to produce a steady state anodic dissolution were performed at 100, 200, 300, 400, and 1000 $\mu A/cm^2$. The potential of the magnesium failed to stabilize after several hours of polarization at these current densities; the general tendency being toward more anodic potentials over the course of the experiment. Immediately after the attempts at anodic stripping, the rest potential was about 0.57 volts cathodic of the reference electrode. As soon as the current was stopped the potential began to drift to more anodic potentials. Evidently, the surface film observed in the anodic polishing experiments prevents a stable surface from forming on the magnesium electrode.

Temperature effects on $Mg(BF_4)_2$ solutions in PC

Magnesium reduction competes with electrolyte reduction during electrolysis of $Mg(BF_4)_2$ solutions in PC. The detection of boron in the cathodic deposits shows that the anion, as well as the solvent, is involved in the cathodic reactions. To evaluate the relative activation energies of these competing reactions, several experiments were performed at temperatures ranging from -60°C to 110°C. Temperatures below 0°C were attained by setting up an airtight, single chamber cell in the glove box and then transferring the cell to an acetone/dry ice bath outside of the glove box. Magnesium foil anodes, platinum foil cathodes, and 0.6 m $Mg(BF_4)_2$ were used in these experiments. At -60°C the electrolyte was sufficiently viscous to block magnetic stirring; in all other experiments the electrolyte was stirred. Figure 2 shows the variation of electrolyte conductivity with temperature. At -60° 23 coulombs were passed at current densities of .48 mA/cm^2 and .03 mA/cm^2 at the anode and cathode respectively; the potential drop averaged about 45 volts. No deposit was detected at the cathode. The anode surface was roughened, but lacked a visible surface film. Based on weight difference, anodic current efficiency was 100%. When a freshly electrodissolved magnesium surface was left in the solution as it warmed to room temperature, the active surface area became coated with a black film. This film resembled the film formed at the anode during ambient temperature electrolysis. At -11°C the higher solution conductivity allowed anodic and cathodic current densities of mA/cm^2 and 0.78 mA/cm^2 respectively; the potential drop was maintained at about 40 volts. A clear gel formed on the cathode. This deposit was sufficiently rigid to have visible cracks and could be pealed off of the cathode in semi-rigid flakes. Magnesium content in the deposit was 4.4 % by weight, which is about twice the concentration in the bulk electrolyte. The anode was coated with small grey spots and had only been dissolved with 24% current

Figure 2. The Conductivity of 0.6 m $Mg(BF_4)_2$ in Propylene Carbonate as a Function of Temperature.



efficiency. Evidently at -11°C the solution is sufficiently warm for the solvent corrosion reaction to be significant.

Experiments conducted at 25°C and above were performed in the glove box. Electrolysis was performed in single chamber glass cells; magnesium rods placed in the center of the cell were used as anodes and concentric aluminum cylinders were used as cathodes. At 25°C anodic and cathodic current densities of 34 and 2.8 mA/cm^2 respectively were maintained with a potential drop of 30 volts. The cathodic deposit was the porous, grey, 10% magnesium deposit described above. The anode was coated with a yellow layer, which was easily wiped off to reveal an electropolished surface. Anodic current efficiency was 100%.

In the final experiments a cell was placed in an oil bath and heated while current was passed. Current was adjusted throughout the experiment to maintain a potential drop of about 20 volts across the cell. During the experiment the anodic and cathodic current densities were increased from initial values of 53 and 2.7 mA/cm^2 to final values of 533 and 27 mA/cm^2, respectively. The experiment was terminated at 110°C when the electrolyte gelled. Solid $Mg(BF_4)_2$ is known to decompose at this temperature and the gelling may be a consequence of reactions between PC and decomposition products of the solute. The cathodic deposit consisted of bright white flakes containing 22% magnesium. The anode was electropolished at 120% current efficiency; an efficiency in excess of 100% indicates some unipositive magnesium dissolution. The magnesium surface was not as shiny as that obtained at 25°C and lacked the yellow surface film associated with ambient temperature electropolishing.

Magnesium reduction does appear to be facilitated by higher electrolyte temperatures, but the enhancement is not of practical significance. Thermal decomposition of the electrolyte puts an upper limit of 100°C on the useful temperature range for $Mg(BF_4)_2$ containing electrolytes. Corrosion of fresh magnesium surfaces at the anode is insignificant at -60°C, but electropolishing does not appear to occur at this temperature. Electropolishing occurs at ambient temperature, but apparently only after the formation of a coherent, yellow surface film. At higher temperatures the surface film is not detected, but the surface, although smooth, is not as shiny as the surface formed at room temperature. It has not been determined whether the lower sheen at the higher temperature is a consequence of the absence of the yellow surface film or of chemical reaction with solute decomposition products.

B. $Mg(BF_4)_2$ in Dimethyl Sulfoxide

$Mg(BF_4)_2$ was also used as a solute in DMSO. A 0.7 m solution of $Mg(BF_4)_2$ in DMSO was compared with a 0.7 m solution of $Mg(BF_4)_2$ in PC. Undivided H cells with magnesium rod anodes and aluminum rod cathodes were used in comparing these electrolytes. The potential drop in both experiments was maintained at about 4 volts and the cathodic densities were 0.05 mA/cm^2 for the DMSO solution and 0.8 mA/cm^2 for the PC solution. The cathodic product in PC was the 20% magnesium, black film described earlier. The cathodic product in DMSO was a blistered, grey film containing only 5% magnesium. Since the donor number of DMSO is twice the donor number of PC, it is to be expected that cation reduction is more difficult in DMSO. No further experiments were performed in DMSO.

C. Magnesium with Decaborane in Tetrahydrofuran

An attempt was made to duplicate Brenner's plating bath based on decaborane[25]. The bath was prepared by slowly adding a saturated solution of 1 gram of decaborane dissolved in anhydrous tetrahydrofuran to 25 ml of a commercially obtained 1.7 molar solution of lithium methyl in diethyl ether. After combination of the two solutions a heavy, yellow layer separated out of the bath. The bath was completed by adding 25 ml of a saturated solution of magnesium chloride in anhydrous tetrahydrofuran. With the addition of the magnesium chloride solution the bath became homogeneous. The bath was electrolyzed at a cathodic current density of 10 mA/cm^2 in a small H cell with a magnesium anode and an aluminum cathode. The cathodic deposit was only 20 percent metallic, with twice as much lithium present as magnesium.

D. $Mg(BF_4)_2$ in Tetrahydrofuran

Before abandoning the study of $Mg(BF_4)_2$ as a solute, a final experiment was conducted using THF as the solvent. This experiment was performed to check if the ether solvent would be less reactive during the attempted magnesium reduction. The THF was dried by storing over 4 Å molecular sieves for 48 hours. This treatment should reduce the water content to less than 20 ppm[70]. A saturated solution of $Mg(BF_4)_2$ in THF (about 0.2 m) was electrolyzed in a small single chamber cell using a magnesium rod as an anode and a copper foil as the cathode. The electrodes were placed approximately 1 cm apart and an average current density of 85 μA was applied for 9 hours. The potential drop across the cell was initially 50 volts and rose steadily with the passage of current. This rise in potential was caused by the formation of a salt film on the magnesium anode. Shaking the film from the anode lowered the potential drop. At the end of the electrolysis the copper cathode was covered with a thin, shiny deposit. Analysis of the deposit by atomic absorption spectroscopy showed that it contained magnesium but, because of the very small amount of material involved in the deposit, it was not possible to determine if the magnesium represented a thin layer of magnesium or an alloy with the copper substrate. There was no indication of solvent breakdown on the cathode surface. Using magnesium bis-organoborates, Gregory was able to electroplate magnesium at current densities five times higher than were used in the present experiments[26]. Gregory may therefore by correct in his belief that highly ionic magnesium compounds, such as $Mg(BF_4)_2$, are more difficult to electroplate than compounds with a fair degree of covalency in the magnesium-anion bond.

The absence of an organic film on the cathode demonstrates that THF is more stable than PC in the presence of electro-reduced magnesium.

VI. $AlCl_3$ Electrolytes in Propylene Carbonate

$AlCl_3$ is a strong Lewis acid which increases the solubility of alkali chlorides in PC by forming complex anions of aluminum and chloride. The use of such solutions as electrolytes for alkali metal plating was studied extensively by Jorné[4]. The electrolytes studied by Jorné were composed of equimolar solutions of $AlCl_3$ and the alkali chloride and the deposits obtained from these baths contained only the alkali metal and showed no inclusion of aluminum. The purity of the cathodic deposit is in part the result of the formation of the $AlCl_4^-$ anion, which complexes all the aluminum present in 1:1 molar solutions of the salts. The alkali chloride/aluminum chloride complexes were formed by either fusing the two salts at high temperature or by dissolving them individually in PC. The first method was preferred since it avoided thermal decomposition of the solution during the extremely exothermic dissolution of $AlCl_3$ in PC. Peled has reported the formation of a similar complex by dissolving $MgCl_2$ in a thionyl chloride solution of $AlCl_3$. The solvation of the divalent magnesium salt required two moles of $AlCl_3$ for each mole of the magnesium salt[65]. At present, the literature contains no reliable data on the existence of similar complexes in PC.

Experimental

$AlCl_3$ (99.99%,Alfa) was sublimed under vacuum. Solutions were prepared in the glove box by chilling PC to almost 0°C and adding $AlCl_3$ slowly to reduce the amount of thermal decomposition resulting from the exothermic dissolution. Solutions of $AlCl_3$ in PC were light pink when newly prepared; the intensity of the coloring increased with $AlCl_3$ concentration. The solution color darkened with aging, but this could be avoided for several weeks by storing the solutions at 0°C. Prior to electrolysis the solutions were dried twice by storing over 3 Å molecular sieves for 24 hours. Dried solutions were filtered through Whatman GF/F glass fiber filters. The PC used in the experiments was distilled under vacuum as described by McIntosh[69]. Distilled PC has water contents of less than 20 ppm. Treatment of salt solutions in PC with molecular sieves leads to water contents on the order of 1 ppm; this does not take into account water which may be intimately coordinated to the ions in solution[69].

Electrolysis was performed in the same glass H cells used in $Mg(BF_4)_2$ experiments. In some of the experiments a glass frit separated the anodic and cathodic chambers. Micropolarization experiments were performed in the same single chamber cells used in the attempted micropolarization experiments of $Mg(BF_4)_2$ solutions. Electrodes for micropolarization experiments were made of magnesium foil strips which had been treated with Kynar insulator to leave 1 cm^2 active areas.

The reference electrode used was the thallium halide/thallium amalgam electrode described by Baucke and Tobias and subsequently used by Jorné and Hanson[4,28,35]. The thallium amalgam was prepared by adding thallium rod to sufficient mercury to form a 20 wt. % thallium amalgam. Complete amalgamation required several days. Impurities in the amalgam floated to the surface, allowing bright, clean amalgam to be withdrawn from beneath the impurity layer. Thallium halide was dried under vacuum at 300°C for 48 hours prior to use in the cell. The thallium amalgam was held in a glass cup which left approximately 1 cm^2 of amalgam surface area exposed. Electrical connection to the potentiostat was made below the surface of the amalgam. A thin layer of the thallium halide salt was sprinkled over the exposed amalgam surface. The salt was dispersed evenly over the surface by tapping the cup lightly. The glass cup was then lowered into a glass buret filled with the electrolyte and the system was allowed to equilibrate for at least 24 hours prior to use. Connection to the working cell was made via a thin teflon capillary between the bottom of the glass buret and the working cell. Entrapment of gas bubbles in these capillaries is a persistent problem in the operation of these electrodes; to purge these bubbles from the system, valves were added to the top of the buret to allow a vacuum line to be connected to the cell.

Since the thallium amalgam reference electrode system is somewhat cumbersome to use, several electrodes based on thin metal wires were investigated as possible alternatives. Baucke and Tobias[28] reported that a thallium chloride/thallium amalgam reference electrode could be prepared by anodizing a fresh thallium surface in a saturated PC solution of the sparingly soluble salt. While not as stable over long periods of time as the amalgam electrode, which is stable for at least a month in most electrolytes, it appeared to be sufficiently stable for use in shorter duration experiments. Three different methods of preparing a TlCl/Tl surface were attempted. The simplest of these involved scraping the oxide layer from the surface of a thallium wire and then immersing the clean surface in concentrated hydrochloric acid. After 10 to 15 minutes the wire was removed from the acid and rinsed with acetone prior to drying under vacuum. The resulting surface was smooth and grey. Two slightly different anodization schemes were tried: one from a saturated solution of $MgCl_2$ and the other from a saturated solution of TlCl. For both of these schemes the thallium surface was scraped clean in the glovebox. In the $MgCl_2$ solution a charge of 0.36 $Coul./cm^2$ was applied at 0.10 mA/cm^2. Following the procedure of Baucke and Tobias[28], 0.36 $Coul./cm^2$ at 0.20 mA/cm^2 was applied in the TlCl solution. The anodized surfaces appeared similar to the acid treated electrode surface, although there was greater variation in color over the surface of the electrode anodized in TlCl solution.

In $Mg(ClO_4)_2$ solution, the wire electrodes stayed within 5 mV of each other over two days, but drifted 65 mV with respect to a thallium chloride/thalium amalgam electrode; initially being about 30 mV anodic of the amalgam electrode and ending about 30 mv cathodic. In $AlCl_3$ solution the surfaces turned white and the potential drifted rapidly. TlCl solubilization by $AlCl_3$ is a possible source of potential drift, but even the use of $AlCl_3$ solutions saturated with TlCl failed to stabilize the potentials. $AlCl_3$ solutions also affected the stability of the amalgam electrode; over a period of two weeks the potential of a TlCl/Tl(Hg) electrode drifted approximately 20 mV cathodically. Because of this, amalgam electrodes used with $AlCl_3$ solutions were not used for longer than one week.

Another possible reference electrode is a clean aluminum surface, which has been used successfully as a reference electrode in low temperature molten salt electrolytes containing $AlCl_3$[71] and in toluene solutions of $AlBr_3$[72]. However, in $AlCl_3$ solutions in PC, freshly exposed aluminum surfaces failed to equilibrate to a steady potential over a period of 5 days.

Attempts to form a soluble complex between $MgCl_2$ and $AlCl_3$ in PC were unsuccessful. When $MgCl_2$ and $AlCl_3$ were heated together at 100°C under helium at one atmosphere pressure, the resulting solid produced a white suspension in PC, which did not resemble the PC solution of either of the pure components. Analysis of this suspension, which was stable over several days, showed that the magnesium and chloride concentrations were on the order of one to two tenths molal, while the aluminum concentration was on the order of a hundredth molal. Attempts to fuse the solids at higher temperatures lead to compounds which were less soluble and produced grey, murky solutions. When $MgCl_2$ was added to a 1.5 molal solution of $AlCl_3$ in PC, very little of the magnesium salt dissolved, but the solution, which had originally been pale pink, became deep red. Apparently there was some interaction between the two salts, but it was not sufficient to solubilize a significant quantity of the magnesium salt. $AlCl_3$ solutions with significant quantities of dissolved magnesium could only be produced by electrodissolving magnesium anodes into the $AlCl_3$ solution.

Magnesium electrodissolution in $AlCl_3$ solutions in Propylene Carbonate

A preliminary attempt to dissolve magnesium was made using a 1.5 m solution of $AlCl_3$ in PC. The magnesium rod used as the anode in this experiment was cleaned with sulfuric acid prior to being transferred to the glove box and then filed in the glove box to remove surface oxide. An aluminum strip served as the cathode and the solution was stirred during electrolysis. The magnesium dissolved with 100% current efficiency, leaving the active surface roughened but free of a visible surface film.

Dark orange, crystalline deposits were formed at the cathode; this may be the same yellow to orange cathodic deposit noted by Jorné in the electrolysis of $AlCl_3$ containing solutions at platinum cathodes[4]. A total charge of 344 coulombs was passed at an average anodic current density of 1.5 mA/cm^2 and an average potential drop of 20 volts. A second dissolution experiment was performed using the same cell configuration, electrolyte concentration, and current density, but without attempting to remove the surface oxide from the magnesium anode. The current efficiency was again 100%, demonstrating that the native oxide did not significantly hinder magnesium electrodissolution.

Subsequent experiments were performed using a fresh 1.0 m solution of $AlCl_3$. Using the same cell as described above, magnesium was dissolved with 100% current efficiency at 2.66 mA/cm^2. As was true in 1.5 m $AlCl_3$ the magnesium surface was rough but clean and the cathode was coated with an orange deposit which colored the electrolyte. In the course of passing 460 coulombs through the cell, the potential drop rose from an average value of 27 volts to 40 volts. Stopping the electrolysis and wiping the cathode clean of the orange deposit restored the original value of the potential drop. Toward the end of the experiment this cleaning became necessary at increasingly short intervals. The change in solution color during electrolysis indicates that the cathodic product is somewhat soluble in PC. Eventually, the orange material begins to precipitate on the anode.

A second dissolution in 1.0 m $AlCl_3$ was performed in an H cell with a glass frit between the chambers. The same electrode materials were used as above, but the cathode used was three times larger than the anode. This was done to lengthen the time that could be allowed between cleaning the cathode and to allow a greater anodic current density, since the cathodic process is rate limiting. 1,130 Coulombs were passed at an average anodic current density of 4.5 mA/cm^2. Current efficiency was again 100%. The presence of the glass frit between chambers prevented the cathodic product from reaching the anode; at the end of the electrolysis the catholyte was dark orange, but the anolyte had only become pale yellow. Based on the weight loss from the anode, the final solution was 0.23 molal in magnesium. As in the previous experiments, the active area of the magnesium anode became roughened.

Magnesium dissolution in the divided H cell was next performed in 0.2 m $AlCl_3$ in the hope of producing a solution in which the magnesium concentration equaled or exceeded the aluminum concentration. Electrodissolution could not be performed as rapidly in the less concentrated electrolyte; this was primarily attributed to the lower conductivity of the 0.2 m solution (4.15 x 10^{-3} siemens/cm for 1 m $AlCl_3$ versus 2.38 x 10^{-3} siemens/cm for 0.2 m $AlCl_3$). 586 coulombs were passed at an anodic current density of 1.4 mA/cm^2. Anodic current efficiency was again 100%. Elemental analysis showed that the majority of the aluminum and magnesium in solution at the end of the electrolysis was in the anolyte, which was 0.32 molal in aluminum and 0.10 molal in magnesium. The catholyte was only .008 molal in magnesium and contained even less aluminum. A total mass balance on the initial electrolyte concentration and anode weight loss confirmed these values. Chlorine was also present in higher concentrations in the anolyte; 1.0 molal versus 0.11 molal. In the anolyte the chlorine concentration was only slightly in excess of the expected 3 to 1 ratio for aluminum chloride. The high concentration of all three elements in the anolyte suggests that both aluminum and magnesium are present in solution in the form of negatively charged, complex chloride ions.

Elemental analysis of the spent electrolyte from the 1.0 m $AlCl_3$ solution shows similar but less extreme variations in elemental concentrations between the anolyte and catholyte. Both the chlorine and aluminum concentrations are only three times more concentrated in the anolyte than in the catholyte, although the magnesium concentration difference is just as large as in the less concentrated electrolyte. Another difference between the 1.0 and 0.2 molal solutions is the character of the cathodic product. In the 1.0 m electrolyte an orange gel is visible on the cathode fairly early in the electrolysis. When removed from solution, this gel retains its liquid character even after several months of exposure to the atmosphere. Elemental analysis of the gel shows it to be 6.9% chlorine, 2.3% aluminum, and 0.08% magnesium. The cathodes used in electrolysis of 1.0 m $AlCl_3$ also develop small, dark grey, adherent, nodules under the orange gel. These nodules are scattered sparsely over the surface, but are most prominent along the edges of the cathode. Elemental analysis shows them to be about 20% metallic and contain roughly six times as much aluminum as magnesium.

In contrast, the cathodic deposit in the 0.2 m $AlCl_3$ electrolyte appears black while forming on the cathode, but appears orange when removed from solution. Eventually this deposit dries completely to form thick, off-white flakes which are 5.7% chlorine, 14% aluminum, and 1.9% magnesium. During electrolysis a grey sediment forms under the cathode. The different character of the cathodic deposits at high and low $AlCl_3$ concentrations suggests that the species present in solution vary with concentration. The possibility of different ionic species at different concentrations has been proposed by Breivogel and Eisenberg[73], who suggested that at lower concentrations $AlCl_2^+$ and $Al_2Cl_7^-$ were the predominant species, while at higher concentrations $AlCl_4^-$ and $Al_3Cl_8^+$ were the predominant ions in solution.

Micropolarization Experiments in $AlCl_3$ Electrolytes

Micropolarization experiments were performed in the cell described for micropolarization experiments with $Mg(BF_4)_2$ solutions. In most of the experiments both electrodes were 1 cm^2 magnesium foils. After the inactive surface of the electrode had been masked with Kynar insulator, the active area was etched in dilute nitric acid, rinsed in distilled, de-ionized water, and dried under vacuum. In some experiments an aluminum foil was used as the cathode. TlCl|Tl(Hg) reference electrodes were used in all of these experiments with the same electrolyte in the reference electrode chamber as in the working cell. Fresh amalgam electrodes in 0.2 m $AlCl_3$ were found to be 68 mV cathodic of fresh amalgam electrodes in 1 m $AlCl_3$. The teflon capillary from the reference chamber to the working cell was kept flush with the magnesium anode. The potential drop between the teflon capillary and the electrode was estimated by measuring the potential drop across the cell using two identical reference electrodes in different positions; depending on the electrolyte concentration, the potential drop across the cell was only 2 to 5 mV at 100 μA. Based on these experiments, the potential drop between the teflon lead and the electrode was estimated to be less than a millivolt.

Aluminum and magnesium cathodes behave very differently in 1.0 m $AlCl_3$ solutions. In even the longest duration micropolarization experiments, less than 1.5 coulombs were passed through the cell. At these charge densities aluminum cathodes develop a yellow surface coating which resembles the cathodic product in longer duration experiments in 1.0 m $AlCl_3$. When current is stopped these coatings liquify and flow off the cathode, leaving a clean aluminum surface. Magnesium cathodes become coated with a rough, black, adherent surface layer. When 0.2 m $AlCl_3$ was used, the magnesium surface was covered with a fine grained, black surface layer. Stable potentials could not be obtained using cathodic polarization since film production, instead of metal reduction, is the predominant cathode reaction.

Most micropolarization experiments were made using anodic currents. Polarization currents from 0 to 100 μA were used. Prior to collecting data, the anode surface was cleaned with a 100 μA current, which was maintained until the electrode potential varied by less than 0.5 mV/minute. The current was then stepped down to 20 μA in 20 microamp increments and from 20 to 0 μA in 5 microamp steps; the current was then returned to 100 μA using the same increments. Potential values stabilized within two to three minutes at each current density. This cycle was repeated three to four times in each experiment; the potential values at given current densities were found to vary by 5 to 10 millivolts over the course of three to four hours of current density cycling. Exchange current densities were calculated using the same equation used by Jorné for the exchange current densities of alkali metals in $AlCl_3$ solutions in PC.

$$i^o = \frac{1}{A}\frac{RT}{nF}\frac{\partial i}{\partial \eta}\Big|_{i=0}$$

Current densities greater than 100 μA were not used since even the poor reproducibility obtained in the 0 to 100 μA range was lost when larger current densities were used. Current densities in the 0 to 20 μA range also had a negative effect on the reproducibility of micropolarization potentials; in this current range a corrosion reaction competes with magnesium electrodissolution. Magnesium foils which were kept at 20 to 100 μA during dissolution were pitted, but clean. Magnesium foils which had been held at 0 to 20 μA were coated with a rough, grey film. Both the concentration of $AlCl_3$ and electrodissolved magnesium in the electrolyte had a significant effect on the stability of the magnesium potential. When anodic current was first applied, the potential jumped about half a volt anodic and then drifted back to more cathodic values. In fresh 1m $AlCl_3$ solutions, 100 $\mu A/cm^2$ current had to be maintained for three hours before the cathodic drift of the potential had slowed to less than 0.5 mV/minute. When the magnesium foil was allowed to equilibrate overnight in a 20 ml solution in which a 1.5 coulomb charge of magnesium had been electrodissolved (approximately 0.2 m in magnesium), only 20 minutes at 100 μA was necessary to achieve the same potential stability. Jorné and Salomon also noted that the potentials of alkali metals in 1.0 m $AlCl_3$ solutions were more stable as the concentration of the alkali metal in solution was increased[4,74]. In 0.2 m $AlCl_3$ the magnesium potential never achieved this degree of stability, even with small amounts of magnesium dissolved in the electrolyte.

The estimated exchange current density of the magnesium foil in contact with 1.0 m $AlCl_3$ with approximately 0.2 molal electrodissolved magnesium is 1.6×10^{-5} Amp/cm^2. Rough values for the exchange current densities in 0.2 m $AlCl_3$ varied between 1×10^{-6} and 4×10^{-6} Amp/cm^2. The value of the exchange current density in 1.0 m $AlCl_3$ can be compared with the values reported by Jorné for alkali metals in contact with 0.25 m solutions of the corresponding alkali chlorides in 1.0 m $AlCl_3$: 7.8 x 10^{-4} Amp/cm^2 for lithium, 1.65 x 10^{-5} Amp/cm^2 for sodium, and 1.48 x 10^{-6} Amp/cm^2 for potassium. The exchange current density for magnesium is almost the same as that for sodium, which occupies the same row in the periodic table.

The electrode potential of magnesium in 1.0 m $AlCl_3$ is not similar to the potentials of the alkali metals. For 0.25 m solutions of the alkali chlorides in 1.0 m $AlCl_3$, the measured potentials for lithium, sodium, and potassium are reported as 2.41790, 2.18750, and 2.47260 volts respectively. In solutions in which the alkali chlorides were only 0.01 m, the potentials were slightly more cathodic at 2.46010, 2.24460, and 2.51085 volts respectively[4]. In contrast the magnesium potential was only 1.03 volts for a solution which was approximately 0.25 m in magnesium and 1.0 m in $AlCl_3$ and 0.89 volts in solutions with almost no electrodissolved magnesium present. Jorné reported six significant digits in his measurements, while the instability of the magnesium potential only justifies the reporting of, at most, three significant digits. The large difference in electrode potentials between magnesium and the alkali metals, as well as the relative instability of the measured potential and the corroded appearance of the magnesium surface, indicates that the measured potential should be attributed to a corrosion reaction between magnesium and the $AlCl_3$ solution.

$Mg(ClO_4)_2$ in Propylene Carbonate

Anodic dissolution of magnesium in 1.0 m $Mg(ClO_4)_2$ was also attempted using the same experimental apparatus as used in the $AlCl_3$ electrodissolution experiments.

In 1.0 m $AlCl_3$ an anodic current density of 4.5 mA/cm^2 could be maintained by using a cathode which was 2.5 times larger than the anode. In 1.0 m $Mg(ClO_4)_2$ an anodic current density of 0.66 mA/cm^2 could only be maintained by using a cathode which was 3.5 times larger than the anode. After electrolysis, the appearance of the anode and cathode were similar to that observed in solutions of $AlCl_3$ in PC; the magnesium anode had been dissolved with 100% current efficiency to leave a roughened surface with no visible surface film and the aluminum cathode was coated with a yellow film.

Solutions of $Mg(ClO_4)_2$ and $AlCl_3$ have similar conductivities[4,75]. The substantially lower currents obtained in the perchlorate solution therefore indicate that the cathodic or anodic processes are much more difficult in the perchlorate solution. Given the similar appearance of the electrodes in $AlCl_3$ and $Mg(ClO_4)_2$ solutions, the electrode reactions in the perchlorate solution may involve the production of chloride ions via the decomposition of perchlorate ions. One possible route for such a decomposition would be the reduction of perchlorate ion to chlorate ion, followed by the thermodynamically favorable disproportionation of chlorate ion to perchlorate and chloride ions.

VII. Miscellaneous Electrolytes

A. $AlBr_3$ Solutions in Toluene

Due to their low dielectric constants and non-polar character, aromatic hydrocarbons are not usually considered suitable solvents for non-aqueous electroplating. With dielectric constants of less than three, aromatic solvents are not effective solvents for ionic salts, but they are capable of dissolving the covalent salt, $AlBr_3$, at concentrations of up to 3 molar[72]. Solutions of $AlBr_3$ have conductivities of only about 10^{-9} siemens/cm, but the solutions they form with alkali halides have conductivities of up to 0.01 siemens/cm. Solutions of the form $MX/AlBr_3/ArH$, where M is an alkali metal, X is a halogen other than fluorine, and ArH is an aromatic hydrocarbon have been extensively studied in recent years by Peled and Gileadi[72,76-78]. Their work with these systems is an extension of pioneering work by Plotnikov in the 1930's in which the usefulness of these systems as a plating bath for aluminum was investigated. In the most recent publications, $AlBr_3$ solutions in benzene, xylene, toluene, or mesitylene were used to dissolve chlorides, bromides, and iodides of the alkali metals. All of these alkali halide salts are soluble in the hydrocarbon solutions at molal ratios of 0.5 moles per mole $AlBr_3$. Lithium halides are an exception, with mole ratios of lithium to aluminum of 0.8:1.0 reported. In addition $CuBr_2$ has been reported to dissolve in a 1:1 ratio with $AlBr_3$. The bromide salts form the species $[M^+Al_2Br_7^-]_n$ in solution, where n represents as many as four coordinating solvent molecules. In toluene this extensive complexation raises the viscosity from a value of 0.5 cP for the pure solvent to 1.9 cP for a solution of 0.76 M KBR in 2.3 M $AlBr_3$. Despite the similarity in chemical structure between the $AlBr_3$/alkali bromide solutions and the $AlCl_3$/alkali chloride solutions in PC, the systems are not completely analogous. In the $AlCl_3$ system the alkali metal ion is the preferred species for reduction and $AlCl_3$ serves to form a complex anion which solubilizes the alkali chloride salt. In most of the $AlBr_3$ systems, aluminum is the primary reduction product and the alkali bromide serves mainly to increase the conductivity of the plating bath. In solutions where the molar ratio of M to $AlBr_3$ is less than 0.5, aluminum deposits at approximately 2 volts cathodic of an aluminum wire reference electrode. When the mole ratio is greater than 0.5, aluminum continues to deposit at about 3.5 volts. As the ratio approaches unity, aluminum is no longer reduced and only the alkali metal appears in the deposit. It is also reported that the difference in reduction potential between aluminum and the metal ion of the halide salt is smaller in the $AlBr_3$/hydrocarbon system than in aqueous or polar non-aqueous solvents; Peled and Gileadi suggest that this makes the aromatic solvent system a good candidate for alloy deposition[78].

Great care must be taken in the preparation of these electrolyte baths. $AlBr_3$ is highly hygroscopic and any water absorbed in the salt reacts to form HBr in the electrolyte, resulting in a yellowing of the clear solution. Although it is impossible to completely avoid some discoloration in electrolyte preparation, keeping moisture in the salt to a minimum improves deposit quality.

An attempt was made to prepare a magnesium analogue of the alkali bromide system. Toluene was dried for several days over 3 Åmolecular sieves, which is reported to reduce water concentration to less then 1 ppm[70]. $MgBr_2$ was baked at 300°C under a vacuum of less than 1 torr for three days. White crystals of $AlBr_3$ were obtained by subliming $AlBr_3$(Alfa,99.99%) under vacuum. All solution preparations and experiments were performed in the glove box under helium atmosphere.

A 0.34 m solution of $AlBr_3$ in toluene was prepared. A light yellow color indicated the unavoidable presence of some HBr in the solution. Sufficient $MgBr_2$ was added to the solution to produce a 0.17 m solution in the magnesium salt. When 24 hours of stirring failed to dissolve all of the magnesium salt, $AlBr_3$ was added to increase the $AlBr_3$ molality to 0.69. After an additional 24 hours of stirring, the solution had formed two layers; a dark brown top layer over an opaque, light brown layer; some $MgBr_2$ still remained undissolved. After increasing the $AlBr_3$ concentration to 1.16 m the last of the $MgBr_2$ went into solution. Immediately following the complete dissolution of the $MgBr_2$, two layers were present in the solution which differed from the layering present prior to complete dissolution: the top layer was identical to the slightly yellow $AlBr_3$ solution and the bottom layer was a dark, opaque, slightly red brown solution. Eventually the upper layer disappeared, but this may have been the result of toluene evaporation during solution handling. The final molar ratio of magnesium to aluminum was 1:7.

Electrolysis of the solution was performed in a simple, single chamber glass cell containing a 1 cm^2 aluminum cylinder working electrode and aluminum wire reference and counter electrodes. The working electrode was activated by applying a 100 μA anodic current for a half hour prior to use. Cyclic voltammograms were featureless between 0 and 3 volts cathodic of the aluminum reference electrode, resembling those reported by Peled and Gileadi[72]. The working electrode was held at 3 volts cathodic of the aluminum reference electrode for 12 minutes at an average current of 13 mA. During this time the counter electrode dissolved to leave a smooth, shiny aluminum surface.

After the electrolysis the working electrode was rinsed with acetone. Most of the electrode surface showed no evidence of electrochemical activity. Only a few rough, grey nodules, which whitened on exposure to air, were present on the surface; the largest of these being about .01 cm^2 in area. Elemental analysis of the nodules showed them to be only 15% metallic by weight, with a 60:1 mole ratio of aluminum to magnesium. Considering that the mole ratio of magnesium to aluminum in the toluene solution is only 1:7 it is consistent with the results of Peled and Gileadi that the deposit is almost entirely aluminum. Since the solubility of $MgBr_2$ is so low in $AlBr_3$ solutions, it is very unlikely that the use of more cathodic plating potentials could significantly increase the magnesium content of the deposit. No further experiments were made with this system.

B. Magnesium Acetate in Dimethyl Sulfoxide

The successful electrodeposition of nickel from DMSO has been reported by Srivastrava and Tikoo[79]. Using 0.3 M nickel acetate in DMSO, crack free, adherent deposits were obtained, while the use of $NiCl_2$ or $Ni(BF_4)_2$ resulted in black, non-adherent deposits. The black deposits were attributed to reduction of DMSO at the cathode. The authors believed that the better performance of the acetate salt was due to a stronger interaction of the acetate anion with the nickel ion, leading to a lower concentration of DMSO molecules at the cathode surface.

Since, like magnesium, nickel is a divalent metal, magnesium acetate in DMSO was investigated as a possible plating bath. Magnesium acetate also was an attractive salt since it can be completely dehydrated without decomposing the salt[80]. A saturated solution of magnesium acetate in DMSO, approximately 0.1 m, was used in an undivided H cell. Using a cathodic current density of only 5×10^{-5} Amp/cm^2, the potential drop between a magnesium anode and an aluminum cathode rose from 4 to 30 volts during the passage of only 14 coulombs. The resulting cathodic deposit was a clear gel which was only 4% magnesium. Magnesium acetate was found to insoluble in PC and no further experiments were attempted with this salt.

C. Molten Electrolytes

Molten dimethyl sulfone and sulfolane have both been investigated as potential solvents for lithium intercalation batteries. Since V_2O_5 has been shown to be an effective host lattice for reversible lithium intercalation in these solvents, Pereira-

Ramos et. al. attempted to form analogous Mg intercalation electrodes[81]. Fairly reversible magnesium insertion was obtained at 150°C using molten solutions of $Mg(ClO_4)_2$ in dimethyl sulfone or $Mg(CF_3SO_3)_2$ in sulfolane. Based on the success of these electrolytes with intercalation cathodes, an attempt was made to plate magnesium onto metal foil electrodes.

Dimethyl sulfone was recrystallized from boiling water, followed by recrystallization from absolute methanol, and then dried and distilled under vacuum. Sulfolane was distilled under vacuum. $Mg(ClO_4)_2$ (Alfa) was dried under vacuum at 200°C for two days. $Mg(CF_3SO_3)_2$ (Alfa) was used as received and only opened under He atmosphere. All solution preparations and electrolysis were performed in a glovebox under He atmosphere.

A 0.37 m solution of $Mg(CF_3SO_3)_2$ in sulfolane was heated to 100°C in an oil bath. The cell used in the experiment was a simple glass cylinder with a magnetic stir bar at the bottom. A platinum foil was used as the cathode and a magnesium foil as the anode. The electrodes were spaced about 0.5 cm apart. The average current density was 0.42 mA/cm^2 at the anode and 0.18 mA/cm^2 at the cathode and the potential drop across the cell averaged between 30 and 40 volts. A total of 5.7 coulombs was passed. After electrolysis, the platinum cathode was covered with an orange gel which resembled the gel produced during cathodic reduction of PC electrolytes containing $AlCl_3$. These orange colored deposits may be the result of cathodic reduction of halogenated species; in this case the fluorine present in $Mg(CF_3SO_3)_2$. The magnesium anode was severely corroded and appears to have been attacked chemically as well as electrochemically. Based on electrode weight loss, a purely electrochemical dissolution would have had 840 percent current efficiency. $Mg(CF_3SO_3)_2$ does not appear to be compatible with the formation of bulk deposits of magnesium.

A 1.0 m solution of $Mg(ClO_4)_2$ in dimethyl sulfone was heated to 115°C. The electrolytic cell was similar to the cell described above. 6.7 coulombs were passed at an average anodic current density of 0.74 mA/cm^2 and an average cathodic current density of 0.43 mA/cm^2. The potential drop across the cell varied from 25 to 40 volts. After electrolysis, the magnesium anode was slightly roughened and darkened. Magnesium was dissolved with 100 percent current efficiency. The platinum cathode was slightly blackened but had no detectable weight gain. The experiment was repeated with a fresh magnesium foil anode and an aluminum foil cathode. 14.1 coulombs were passed at an anodic and cathodic current density of 0.68 mA/cm^2. The voltage drop and anodic behavior were similar to those of the previous experiment, with the exception of the development of a few small, black nodules at the edges of the aluminum cathode. These nodules resembled the spots observed at the cathodes in 1 m $AlCl_3$ solutions in PC. No further experiments were performed with these solvents.

D. Room Temperature Fused Salt Baths

In addition to the conventional non-aqueous electrolytes consisting of metal salts in polar solvents, room temperature non-aqueous electrochemistry has also been performed using low temperature fused salt systems. One of the first low temperature fused salt baths to be used for electroplating metals was the mixture of $AlCl_3$ with alkyl pyridinium chlorides. Although aluminum was quasi-reversibly reduced in these systems, the deposit quality deteriorated due to reaction between the fresh deposit and the alkyl pyridinium cation[82,83]. Wilkes et. al. improved upon this system by screening a number of organic cations on the basis of theoretically calculated electron affinities[84]. 1,3 dialkyl imidazolium salts were selected as the most promising co-salts for the melt and a homologous series ranging from 1-methyl-3-methyl imidazolium chloride to 1-methyl-3-butyl imidazolium chloride (MBICl) was prepared. Melts of these salts with $AlCl_3$ had reduction potentials which ranged from 0.6 to 1.0 volts more cathodic than that of butyl pyridinium chloride melts and the new melts proved to be much less reactive with aluminum deposits. Although Wilkes obtained his best results using 1-methyl-3-ethyl-imidazolium chloride (MEICl), Gifford and Palmisano[71] report that the larger alkyl groups give more stable melts and attribute this behavior to the stabilizing effect of alkyl substituents with greater electron donating ability. Gifford and Palmisano were also able to extend the cathodic limit of the melt a further 500 mV by using trialkylimidazolium salts.

Chloro-aluminate/imidazolium fused salts are liquid at room temperature between

$AlCl_3$ mole fractions of 0.40 and 0.67[84]. Thianthrene, ferrocene, $CuCl_2$, and $TiCl_4$ are reported to be soluble in the melts. At $AlCl_3$ mole fractions lower than 0.5 the melt is basic and is formed by the equilibrium:

$$MEI^+ + Cl^- + AlCl_3 = MEI^+ + AlCl_4^-$$

The cathodic reaction in these melts is the reduction of the imidazolium cation. At $AlCl_3$ mole fractions greater than 0.50 the melt is formed by:

$$MEI^+ + AlCl_4^- + AlCl_3 = MEI^+ + Al_2Cl_7^-$$

and aluminum is the cathodic reduction product[85]. MEICl is also capable of forming room temperature melts with CuCl at CuCl mole fractions between 0.33 and 0.67[86,87] and with $GaCl_3$ at mole fractions between 0.3 and 0.7[88]. A bromine analogue of the aluminum chloride melt has been reported; $AlBr_3$ forms a room temperature melt with MEIBr at mole fractions between 0.30 and 0.71[89]. As is true for the chloride melts, aluminum is reduced when $AlBr_3$ is present at mole fractions greater than 0.5.

Experimental

99% 1-methyl-imidazole (Alfa) was distilled under vacuum, removing the colored impurities. Chloroethane (b.p. 13°C,Kodak) was purchased as a pressurized liquid. All syntheses were performed in the glove box under a He atmosphere. 1-methyl-3-ethyl imidazolium chloride (MEICl) was prepared according to the method of Gifford and Palmisano[71] by adding a four fold molar excess of chloroethane to 1-methyl-imidazole in a metal pressure vessel. The vessel was kept at 80°C for one week. Excess chloroethane was bled out of the reaction vessel, leaving a dry white solid. 1-methyl-3-butyl-imidazolium chloride was prepared in a similar manner using chlorobutane (b.p. 78°C,Kodak). Because of the higher boiling point of chlorobutane, this reaction could be carried out in a glass pressure vessel. After one week at 80°C, the reaction vessel was connected to a vacuum line and pumped down to remove the excess chlorobutane.

$MgCl_2$ was added to MEICl, but did not spontaneously form a melt. MEICl was next heated to 130°C and melted to form a slightly green, clear liquid. Sufficient $MgCl_2$ was added to the melt to form a mixture with a 0.44 mole fraction of the magnesium salt, but no interaction between the two salts was evident. After one day of contact, the mixture was diluted by adding sufficient MEICl to form a 1.4 molal solution of $MgCl_2$ (0.0017 mole fraction $MgCl_2$). When this mixture was stirred, a beige, milky solution or suspension was formed. Cooling this mixture to room temperature produced a light pink solid over a layer of sedimented $MgCl_2$. Since the color change indicated some interaction between MEICl and $MgCl_2$, the solution was diluted further with sufficient MEICl to have formed a 1 m solution if all the $MgCl_2$ went into solution. This mixture was heated to 90°C and electrolyzed in a single chamber glass cell using a magnesium foil anode and a platinum foil cathode. 55 coulombs were passed through the cell at an average anodic current density of 10.3 mA/cm^2 and an average cathodic current density of 8.3 mA/cm^2. The potential drop across the cell averaged between 10 and 20 volts. This potential drop is substantially lower than what is observed at similar current densities in liquid organic solvents and is attributed to the ionic character of the MEICl solvent. After electrolysis the magnesium foil anode was highly corroded. Based on weight loss, magnesium was dissolved with 85% current efficiency, but the final electrode weight was probably increased by corrosion products adhering to the surface. The platinum cathode was covered with a dark orange, non-adherent deposit; this deposit was soluble in hexane and looked similar to the cathodic product in 1 m solutions of $AlCl_3$ in PC. This similarity suggests that the orange solid is a product of the reduction of chlorine containing species.

In a second experiment, the cathode metal was changed. A magnesium foil anode and a copper foil cathode were immersed in a 0.96 m mixture of $MgCl_2$ and MEICl at 90°C. The copper electrode was pretreated by rinsing in nitric acid, sulfuric acid, and distilled water and then dried under vacuum. 146 coulombs were passed through the cell at average current densities of 10 mA/cm^2 at the anode and 25 mA/cm^2 at the cathode. The potential drop across the cell was similar to the drop in the previous experiment. The magnesium anode was heavily corroded with a calculated current efficiency of only 65%. The deposit at the copper cathode appeared identical to the deposit produced on the platinum cathode. Cleaning the orange deposit off of the electrode revealed a porous, green coating on the copper surface. Elemental analysis of the green film showed it contained 4.5% magnesium and 40.5% copper. Apparently, electrically reduced magnesium is chemically oxidized at the copper surface.

Electrolysis was also performed using molten MEICl with $Mg(BF_4)_2$ as the magnesium salt. A 0.51 m solution of $Mg(BF_4)_2$ was heated to 100°C. A magnesium foil anode and copper foil cathode were placed about 0.5 cm apart. In addition to acid pre-treating the copper cathode, the side facing the anode was filed inside the glove box in an attempt to remove surface oxide. 138 coulombs were passed through the cell at average current densities of 43 mA/cm^2 at the anode and 92 mA/cm^2 at the cathode. The potential drop across the cell varied between 5 and 10 volts. Apparently this solution has a much higher conductivity than the $MgCl_2$ solution, which probably reflects a much greater degree of dissociation of the fluoroborate salt in MEICl. The solubility of $Mg(BF_4)_2$ in room temperature MEICl/$AlCl_3$ melts seems to bear this out. During electrolysis the mixture changed color: initially the mixture had a lime green color similar to that of pure, molten MEICl; during electrolysis the solution turned reddish brown and began to darken. About 110 coulombs into the experiment the dark color became pronounced and the potential drop began to rise quickly from 6 to 10 volts. Considering the temperature of the electrolyte, the deterioration of the conductivity is probably due to thermal decomposition of the fluoroborate anion. After the experiment a white sediment was found on the bottom of the cell. Similar sediments are observed in PC solutions made with $Mg(BF_4)_2$ which has undergone some thermal decomposition during vacuum drying. The magnesium anode was electrodissolved with 100% current efficiency and, although much of the surface looked corroded, there were regions where the magnesium appeared electropolished. This was the only MEICl based solution which gave any indication of magnesium electropolishing. The cathodic deposit looked identical to that produced at the copper cathode in the $MgCl_2$ solution, with no apparent difference between the filed and unfiled electrode faces.

The previous experiment was repeated using a platinum foil cathode and a fresh 0.58 m mixture of $Mg(BF_4)_2$ in MEICl maintained at 80°C. 127 coulombs were passed at average current densities of 24 mA/cm^2 at the anode and 35 mA/cm^2 at the cathode. The potential drop was initially about 6 volts, but rose dramatically as the solution color changed from lime green to reddish brown. This discoloration occurred more rapidly than in the previous experiment performed at 100°C with a copper cathode. Apparently thermal decomposition is not the only factor in the bath deterioration. Since the major difference in the two experiments is the cathode material, it is possible that a cathodic reaction product is responsible for the color change. Once solution color had changed, the potential drop could only be maintained at less than 20 volts by gradually reducing the current density. After electrolysis the magnesium anode appeared more severely corroded than in the 100°C experiment and only a few very small regions of shiny magnesium were visible. The anodic current efficiency was only about 76 percent. At 80°C there should have been very little thermal decomposition of fluoroborate anion and it may be that decomposition products are important in electropolishing magnesium in molten MEICl. The platinum cathode was coated with the usual gel-like, dark orange deposit observed in chloride containing electrolytes. It is possible that this deposit is somewhat soluble in MEICl and is responsible for the observed color change; this would be analogous to the cathodic behavior or $AlCl_3$ solutions in PC.

$AlCl_3$/MEICl and $AlCl_3$/MBICl

The room temperature $AlCl_3$/MEICl and $AlCl_3$/MBICl systems were also investigated as possible solvents for $MgCl_2$ and $Mg(BF_4)_2$. The fused salts were prepared by cooling the MEICl or MBICl and $AlCl_3$ to about 0°C on a cold plate in the glove box. When the organic salt and $AlCl_3$ were combined the liquid molten salt formed upon contact, although several days of stirring were usually required for complete liquification of the salts. Wilkes cooled his salts with liquid nitrogen and was able to obtain virtually colorless melts[84]. At the temperatures obtainable on the cold plate, some brown discoloration could not be avoided. As was reported by Gifford and Palmisano[71], the more acidic melts were darker brown. It was also found that storing the melts on the cold plate did not prevent the melts from darkening over two or three days.

$MgCl_2$ was added to a neutral $AlCl_3$ melt with $AlCl_3$ mole fraction of 0.53. With only 1 mole of $MgCl_2$ added per 11 moles of $AlCl_3$, no dissolution of $MgCl_2$ was observed after 24 hours of stirring. Sufficient $AlCl_3$ was added to the mixture to produce an acidic melt with $AlCl_3$ mole fraction of 0.61. After a further 24 hours of stirring the mixture was a cloudy brown suspension; $MgCl_2$ settled out of the suspension when the stirring was stopped. The melt was then made basic by adding sufficient MEICl to reduce the $AlCl_3$ mole fraction to 0.44. This solution turned cloudy green after 24 hours of stirring, but there was still an appreciable amount of undissolved $MgCl_2$. The green color was found to be characteristic of very basic melts of $AlCl_3$/MEICl and did not reflect any interaction between $MgCl_2$ and the melt.

Acidic melts of MBICl were prepared with an $AlCl_3$ mole fraction of 0.7. These melts were found to be capable of dissolving one half mole of $MgCl_2$ for each mole of $AlCl_3$. A melt containing the maximum concentration of $MgCl_2$ was electrolyzed using a magnesium rod anode and a nickel foil cathode. 21 coulombs were passed through the cell at an average cathodic current density of 0.33 mA/cm^2. During the experiment the electrodes were 0.5 cm apart and the average value of the potential drop was 6 volts. The cathode became coated with a dark grey deposit which contained twice as much aluminum as magnesium.

$Mg(BF_4)_2$ was also added to $AlCl_3$/MBICl melts with an $AlCl_3$ mole fraction of 0.7. $Mg(BF_4)_2$ was soluble in this melt, but the viscosity of the resulting solution increased with increasing fluoroborate salt concentration. A 1.5 molal solution of $Mg(BF_4)_2$ was too viscous to be stirred with a magnetic stirrer. At this concentration the molar ratio of magnesium to aluminum was 2.6:1.0. Electrolysis of such a solution would probably result in a magnesium/aluminum alloy with a high concentration of aluminum.

VIII. Conclusions

Although none of the systems studied in this investigation produced suitable magnesium deposits, several of them are probably worth further attention. Aromatic solvents should probably be studied further, since they lack the functional groups which are attacked by such reactive species as the unipositive magnesium species present in Grignard reagents. Although the attempt at $AlBr_3$-$MgBr_2$ complexation was unsuccessful, there are other systems which are capable of forming moderately well conducting solutions at temperatures between 25°C and 150°C using substituted ammonium salts with tetrafluoroborate, perchlorate, or hexafluorophosphate anions[90]. Some of these other systems might be capable of dissolving magnesium salts.

Also, although the room temperature $AlCl_3$/alkylimidazolium chloride salt failed to produce a suitable bath for electroplating magnesium, there are analogous ambient temperature $AlBr_3$/alkylimidazolium bromide molten salt systems[89]. The chemistry of $AlCl_3$ and $AlBr_3$ is sufficiently different (e.g. $AlBr_3$ is soluble in toluene while $AlCl_3$ is not) that the $AlBr_3$/imidazolium bromide melt is worth studying as a possible solvent for magnesium salts.

To date, ambient temperature magnesium electrodeposition has only been performed in ether solutions. Most of the successful attempts at deposition, including some of the recent work by Gregory, have involved the reduction of magnesium from the unipositive alkyl magnesium component of the Grignard reagent, however successful deposition is not limited to Grignard based electrolytes[26]. Brenner produced several magnesium/boron alloys with high magnesium contents using aluminum hydrides and borohydrides and claimed to have produced a pure magnesium deposit using an unknown magnesium-boron compound derived from magnesium chloride, decaborane, and lithium methyl. Brenner also produced this bath using decaborane and a Grignard reagent as starting materials[25]. In the present investigation, although $Mg(BF_4)_2$ failed to produce a metallic magnesium deposit in PC solution, this salt could be used to produce a thin layer of electrodeposited magnesium when dissolved in THF. Gregory also found that magnesium could be deposited from THF solutions of magnesium bis-organoborates ($Mg(BR_4)_2$). Gregory believed that it was important for the magnesium atom to be involved in a bond with a high degree of covalent character for deposition to take place. However, I found that the ionic salt, $Mg(BF_4)_2$ could also be used in THF for magnesium plating, although the current density was much lower than Gregory was able to reach using the magnesium bis organoborate complexes.

Although Gregory may be correct in his belief that a degree of covalent character in the magnesium bond of the solute molecule is helpful in electrodepositing magnesium, I believe that the chemical stability of the solvent molecule is of equal importance. The Grignard reagent is unique to ethereal solvents; all of the other common classes of organic solvents (including cyclic esters such as PC), are decomposed by reaction with the unipositive RMg^+ ion. During electro-reduction of magnesium salts in other solvents it is possible that a unipositive magnesium species is produced at the cathode; such a species would not necessarily need to be of the form RMg^+ to have a similar reactivity with the solvent. Chemical compatibility with Grignard reagents would probably be a good screening test for selecting solvents for magnesium electrodeposition.

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